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Desulfurization of gypsum

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DESULFURIZATION OF GYPSUM

by

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ABSTRACT

The thermodynamic and kinetic feasibility of decomposing gypsum into sulfur dioxide and calcium oxide by application of heat alone (thermal decomposition) and by application of heat and a reducing gas (reductive decomposition) was investigated. The purpose was to determine whether thermal or reductive decomposition could be used for a commercial process.

Examination of the reaction equilibria showed that reductive decomposition was thermodynamically feasible but thermal decomposition was questionable. On the other hand, the kinetic feasibility of reductive decomposition was uncertain because of side reactions which could lead to the formation of calcium sulfide.

In a laboratory study samples of crushed and sized gypsum were heated in a controlled atmosphere while suspended from a weighing balance. When a nitrogen atmosphere was employed, the gypsum decomposed fairly rapidly at temperatures in the range of 2200 to 2300°F. However, the presence of small amounts of the decomposition products, sulfur dioxide and oxygen, in the atmosphere either prevented the decomposition or reduced the rate of decomposition to a negligible value. Hence thermal decomposition is considered impractical.

When a reducing gas such as carbon monoxide was mixed with carbon dioxide, sulfur dioxide, and nitrogen and then passed over gypsum heated to about 2200°F, the decomposition was generally rapid. The rate of decomposition was found to be a function of the temperature, mass velocity, particle size and gas composition. It was also shown that the amount of calcium sulfide formed was a function of the temperature and gas compo-

sition. Conditions were determined which would yield almost complete desulfurization, a relatively fast rate of decomposition, and a negligible amount of calcium sulfide. Thus when a gas mixture composed of 4 per cent carbon monoxide, 20 per cent carbon dioxide, 5 per cent sulfur dioxide, and 71 per cent nitrogen was passed over -7 +8 mesh particles of gypsum at 2200°F, the desulfurization was rapid and complete and the amount of calcium sulfide produced was negligible. Hence it is concluded that reductive decomposition is feasible.

In order to demonstrate one type of process based on reductive decomposition a pilot plant scale shaft furnace was built and operated in a semicontinuous manner. During the most successful period of operation gypsum was introduced at a rate of 12 pounds per hour and 89 per cent desulfurization occurred. An off-gas containing 2.8 per cent sulfurous gases, believed to be principally sulfur dioxide, was produced along with by-product lime containing 3.1 per cent calcium sulfide. Although these results did not appear economically attractive, further improvement seemed possible since the optimum conditions of operation were not determined.

INTRODUCTION

An adequate supply of sulfur is essential to American industry for sulfur is one of the basic raw materials. Considering tonnage consumed sulfur ranks as one of the ten leading minerals. In 1955 alone Gulf Coast mines, employing the Frasch process, supplied 5,790,000 long tons of sulfur of which 27.6 per cent was exported (26). The rest was used domestically, along with sulfur derived from low-grade ores, pyrites, smelter gases, refinery gases, and natural gas, so that the total equivalent sulfur consumed in the United States was 5,797,000 long tons having a value of about $150,000,000. Of the total, 78 per cent was converted into sulfuric acid which is the cheapest and most widely used acid.

At the present time sulfur mined by the Frasch process dominates the United States and world markets because it is readily available at low cost and is relatively pure, 99.5 per cent or better. Shipping costs and acid conversion costs are lower than for less pure materials. In general, an acid plant using Frasch sulfur requires less fixed capital investment than one of the same size using pyrites.

The only known sulfur deposits which can be mined by the Frasch process are associated with salt domes occurring near the coast of the Gulf of Mexico, and for many years only deposits in Texas and Louisiana were mined. However, in 1954 exploitation of deposits on the Isthmus of Tehuantepec in Mexico began and about 1,000,000 long tons were mined in 1957 (6). Since this production is greatly in excess of Mexican needs, most of the sulfur is supplied to the world market. This supply has

broken the United States producers' monopoly on salt-dome sulfur. Domestic producers' stocks are now reported to be at a record high.

The sulfur supply has not always been so plentiful. After the invasion of South Korea in 1950, the demand considerably exceeded the supply and government allocation was resorted to. Production capacity rapidly increased, though, and domestic controls were removed in 1952. The foreign market was more severely affected. Prices soared on foreign-produced sulfur. Britain, which had become dependent upon Frasch sulfur for over half her supply, had to face a reduction of one-third in imports from the United States. The shortage caused her to undertake the construction of two large plants for manufacturing sulfuric acid from indigenous anhydrite, using a process which concomitantly produces Portland cement and which has been used by Imperial Chemical Industries, Ltd. at Billingham for many years.

In America the temporary shortage served the purpose of focusing attention on sulfur resources and future requirements. The President's Materials Policy Commission (53) estimated that between 1950 and 1975 consumption of sulfur would increase 110 per cent both in the United States and in the rest of the free world. It also estimated that if the industry supply pattern did not change, about 180,000,000 long tons of salt-dome sulfur would be needed in this period. The Commission concluded that reserves of Frasch sulfur would be inadequate since they were judged to be on the order of 100,000,000 long tons. Since then the Mexican deposits with reserves of about 80,000,000 long tons have been developed (4). At the same time offshore deposits in the Gulf of Mexico have been undergoing exploration. One of these, known as the Grand Isle deposit,

is believed to contain 40,000,000 long tons of sulfur (5). The most recent estimates place the reserves of salt-dome sulfur at between 150,000,000 and 200,000,000 tons (6).

Since it appears that the United States will become dependent on offshore and Mexican deposits in the future, it would seem appropriate to consider other sources of sulfur. Of several possibilities, deposits of gypsum and anhydrite, which are naturally-occurring minerals of calcium sulfate, seem to offer the largest and most widely distributed reserves. The President's Materials Policy Commission described these reserves as unlimited.

As previously mentioned, there are plants operating in Europe which utilize gypsum or anhydrite for the simultaneous production of sulfuric acid and cement. Valleroy (52) has prepared a preliminary cost analysis for a plant of this type assumed to be located in South-central Kansas. His studies showed that a plant having a capacity of 200,000 tons per year each of sulfuric acid and cement should produce acid for about the same cost as a conventional acid plant operating on Frasch sulfur. Smaller plants would not be competitive, probably because small cement plants are not competitive. To provide operating flexibility during periods of market unbalance facilities would be needed for producing more of one product than of another. Consequently, Valleroy assumed that the fixed investment would be equivalent to that required for building separate plants for the two products. Since neither the raw material nor the products could absorb much in the way of shipping costs, it would be necessary to locate such a plant near a large source of gypsum or anhydrite and close to markets for both products. This, coupled with the

very large production capacity required, severely limits the areas of application for the process.

In an attempt to develop a commercially feasible process for recovering sulfur from gypsum research was undertaken several years ago by Bollen (12) at Iowa State College. The process envisioned was the decomposition of gypsum at temperatures below that of fusion into lime and an off-gas convertible into sulfuric acid. It seemed advantageous to produce lime rather than Portland cement as the solid by-product since lime is used widely in the agricultural, construction, and manufacturing industries. This was expected to lead to process simplification and reduced raw material requirements which would result in lower capital and production costs.

In the proposed process the key step was the decomposition of gypsum. While working on this Bollen (12) demonstrated that gypsum decomposed rather rapidly in a small, batch, fluidized bed reactor fed with the hot products of combustion from burning natural gas. By varying the air to natural gas ratio the fluidizing gas was made oxidizing, neutral, or reducing. The best results were obtained when the stoichiometric amount of air required for complete combustion of the natural gas was used. An oxidizing gas reduced the decomposition rate while a reducing gas resulted in a solid by-product having considerable calcium sulfide. Some of this contaminant was even present in the solids from runs in which a supposedly stoichiometric amount of air was used. The calcium sulfide was undesirable because it reduced the quality of the by-product lime and the proportion of sulfur recovered. Bollen showed that the sulfide content of the solid could be reduced by subjecting the

material to an oxidizing roast.

Before the feasibility of the new process could be assured many questions had to be answered. Not least of these was the question of whether or not the concentration of sulfur dioxide or other sulfurous gases in the off-gas would be high enough for use in an acid plant.

To demonstrate the process, a small shaft furnace constructed much like a lime kiln was built and operated as part of the present investigation. The first results were discouraging since complete decomposition of the gypsum was not obtained and the by-product lime was seriously contaminated with calcium sulfide. It became evident that additional basic information was needed about the process reactions. Hence, an investigation of the thermodynamics and kinetics underlying some of the important reactions was initiated to develop equilibrium and rate information.

Two possibilities were studied. One involved thermal decomposition of calcium sulfate; the other involved reductive decomposition.

Thermal decomposition takes place by the application of heat alone. At a sufficiently high temperature calcium sulfate decomposes by the following highly endothermic reaction:

$$CaSO_4 = CaO + SO_2 + \tfrac{1}{2} O_2 \qquad (1)$$

For this reaction to be utilized commercially both the equilibrium and rate of reaction would have to be favorable at some temperature below the melting point of the solids, since fusion or sintering would add to the processing difficulties and probably reduce the quality of the lime.

Because of inconsistencies reported in the literature regarding the

equilibrium of Reaction 1 and because of the lack of information concerning the decomposition rate, it was necessary to investigate both the equilibrium and the rate in order to find out whether thermal decomposition was practical or not.

Reductive decomposition is based on the decomposition of calcium sulfate by the simultaneous application of heat and a reducing gas. Decomposition is presumed to take place at high temperatures in accordance with the following endothermic reaction when carbon monoxide is the reducing gas:

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad (2)$$

The corresponding reaction when hydrogen is the reducing gas is

$$CaSO_4 + H_2 = CaO + SO_2 + H_2O \qquad (3)$$

Bollen (12) calculated the equilibrium constant for Reaction 2 and found it favorable. However, his work with a fluidized bed reactor employing reducing conditions indicated that side reactions could lead to the formation of considerable calcium sulfide in the solid by-product. Examples of such side reactions are the following:

$$CaSO_4 + 4\ CO = CaS + 4\ CO_2 \qquad (4)$$

$$CaSO_4 + 4\ H_2 = CaS + 4\ H_2O \qquad (5)$$

Although an oxidizing roast might eliminate the sulfide after it was formed, it is desirable to prevent its occurrence. Therefore, the emphasis was placed on searching for conditions which would promote the princi-

pal desulfurization reactions at the expense of the side reactions.

Two approaches were used. One involved calculating the equilibrium conversion for different combinations of calcium sulfate and reducing gases. The other involved an experimental investigation of the factors influencing the conversion and decomposition rate.

In addition, work on the pilot plant shaft furnace was resumed. The purpose was to demonstrate the utility and appropriateness of this type of equipment for the process.

In summary, the present investigation involved several aspects of the more general problem of developing a process for the production of lime and sulfur dioxide from gypsum. The specific objectives were as follows:

1. To determine the thermodynamic and kinetic feasibility of thermal decomposition.
2. To determine the thermodynamic and kinetic feasibility of reductive decomposition.
3. To determine appropriate conditions for decomposition once the feasibility of either decomposition method was demonstrated.
4. To determine the suitability of a shaft furnace with countercurrent flow of gases and solids for carrying out the decomposition process.

REVIEW OF THE LITERATURE

Methods for recovering the sulfur in gypsum and anhydrite have long been sought in European countries. At the time of World War I, Germany, which was largely dependent on imported pyrites for her sulfur supply, devoted a great deal of research to the problem, since indigenous deposits of gypsum and anhydrite were plentiful. Before the War ended several processes had been developed and used in Germany and many patents and reports subsequently appeared in the literature. Homus (33), Mellor (40), Wyld (55, 56), and numerous other authors (18, 28, 38, 41, 42, 49) have extensively reviewed this literature.

There were essentially two important groups of processes investigated. The first involved thermal decomposition of gypsum, frequently with the addition of one or more substances such as silica, alumina, clay or carbon designed to increase the decomposition pressure. The second group of processes involved reducing gypsum to calcium sulfide by heating it with coal or coke or a reducing gas. The calcium sulfide was treated in one of several ways. One treatment involved passing superheated steam over red hot calcium sulfide to produce calcium oxide and hydrogen sulfide according to this reaction

$$CaS + H_2O = CaO + H_2S \qquad (6)$$

Another involved heating calcium sulfide with calcium sulfate and desulfurizing both materials according to the reaction

$$CaS + 3\ CaSO_4 = 4\ CaO + 4\ SO_2 \qquad (7)$$

Still another consisted in treating an aqueous suspension of calcium sulfide with magnesium chloride and steam as follows:

$$CaS + MgCl_2 + 2\ H_2O = Mg\ (OH)_2 + CaCl_2 + H_2S \qquad (8)$$

A somewhat similar process was also used in which calcium sulfide was treated with water and carbon dioxide in this manner:

$$CaS + CO_2 + H_2O = CaCO_3 + H_2S \qquad (9)$$

Although many processes were proposed, only one survived the post war period, and that was the one developed at Leverkusen, Germany, by Farbenfabriken vorm. Friedrich Bayer and Company. This process served as the basis for the large plants built by Imperial Chemical Industries, Ltd. at Billingham, England, in 1929 and by I. G. Farbenindustrie A. G. at Wolfen, Germany, in 1938. Several other European plants have since been built. Many articles and reports (3, 7, 8, 10, 17, 24, 30, 52) have described the process but Hull and others (34) have recently written one of the more detailed accounts.

The process is carried out at Billingham in the following manner. A mixture of anhydrite, sand, coke, and ashes containing alumina are heated together in large rotary kilns. It is believed that part of the calcium sulfate is reduced to calcium sulfide by the following reaction:

$$CaSO_4 + 2\ C = CaS + 2\ CO_2 \qquad (10)$$

The calcium sulfide in turn reacts with the remaining calcium sulfate to form lime and sulfur dioxide thusly:

$$CaS + 3\ CaSO_4 = 4\ CaO + 4\ SO_2 \qquad (7)$$

The lime then reacts with the acidic oxides to form cement clinker as follows:

$$CaO + x\ Al_2O_3 + y\ SiO_2 + z\ Fe_2O_3 = CaO(Al_2O_3)_x\ (SiO_2)_y\ (Fe_2O_3)_z \qquad (11)$$

After leaving the kiln at around 1400°C the clinker is further processed into Portland cement. The kiln gas contains about 9 per cent sulfur dioxide and passes through an elaborate purification system before it is converted into sulfuric acid in a conventional contact plant.

A survey of the large body of literature dealing with the utilization of sulfur in gypsum and anhydrite indicated four specific areas bearing more or less directly on the present investigation. These included:

1. the forms of calcium sulfate and its hydrates which are stable at different temperatures.
2. the decomposition of calcium sulfate both with and without additives at high temperatures.
3. the effect of reducing gases on calcium sulfate at high temperatures.
4. the oxidation of calcium sulfide.

These areas of the literature are reviewed in detail below.

Calcium Sulfate and Its Hydrates

There are several compounds and different forms of these compounds which can exist in the system involving calcium sulfate and water. Kelley et al. (37) found the literature on this subject in a state of great

confusion. They finally concluded that the following forms were unique and reproducible:

$CaSO_4 \cdot 2\ H_2O$

α - $CaSO_4 \cdot \frac{1}{2}\ H_2O$

β - $CaSO_4 \cdot \frac{1}{2}\ H_2O$

α - soluble anhydrite

β - soluble anhydrite

insoluble anhydrite

The first and last forms correspond to the naturally occurring minerals gypsum and anhydrite respectively. The alpha hemihydrate can be prepared by heating the dihydrate either in water above 97°C or in saturated steam. On the other hand, if the dihydrate is heated in a vacuum to 100°C or in an atmosphere of superheated steam, the beta hemihydrate is formed. The two soluble anhydrites can be prepared by dehydrating the corresponding hemihydrates in a vacuum at about 100°C. The beta soluble anhydrite can also be obtained by the rapid calcination of gypsum at around 200°C. Heating any of the first five forms for an hour at about 900°C will produce the insoluble anhydrite. According to Kelley et al. (37), the two hemihydrates have similar crystal structures while the structures of the two soluble anhydrites have not been completely worked out. Of course, both gypsum and insoluble anhydrite have well known structures.

Newman (43) investigated the behavior of insoluble anhydrite in air at temperatures up to 1545°C by means of differential heating and cooling curves. He was able to confirm the reversible transition of the ordinary form of insoluble anhydrite to a high temperature modification at 1214°C.

The last form was unstable below the transition temperature and could not be studied at room temperature. Newman also found another reversible thermal effect at approximately 1365°C. He believed this to be the melting point of a eutectic mixture of the high-temperature form of anhydrite and calcium oxide. Apparently only a small percentage of the eutectic mixture was calcium oxide and this was provided by the partial decomposition of the anhydrite.

Differential thermal-analysis curves were obtained by Gruver (29) for both gypsum and anhydrite heated in air from room temperature up to 1450°C. The curve for gypsum exhibited a large endothermic heat effect between 100° and 300°C representing the loss of water of hydration. A small unexplained exothermic effect was noted at 370°C and the endothermic effect corresponding to the transition of anhydrite into the high temperature modification was observed at 1230°C. An endothermic effect corresponding to the melting of the eutectic was recorded at 1350°C. The curve for anhydrite exhibited only the transition at 1230°C and melting of the eutectic at 1360°C.

West and Sutton (54) also applied the differential thermal analysis technique to the study of gypsum. They obtained basically the same thermogram for gypsum heated in air as did Gruver (29) but with more detail. Thus they were able to distinguish separate endothermic peaks at 180°C and 215°C caused by the loss of $1\frac{1}{2}$ and $\frac{1}{2}$ molecules of water respectively. Furthermore, they explained an exothermic peak at 360°C as due to the transition of soluble into insoluble anhydrite. Although Gruver noted the same heat effect at 370°C, he was not able to offer an explanation. West and Sutton observed that thermograms of gypsum heated

in nitrogen or carbon dioxide were similar to the thermogram in air.

Decomposition of Calcium Sulfate

The behavior of gypsum alone and in the presence of fluxes at elevated temperatures was investigated by Hofman and Mostowitsch (32). They found that calcium sulfate began to dissociate at 1200°C into calcium oxide, sulfur dioxide and oxygen. Both the rate and degree of dissociation increased as the temperature was raised, and the mixture of calcium sulfate and calcium oxide fused at 1360°C. However, the dissociation was incomplete even when a sample was heated for 20 minutes at 1400°C. Addition of silica to calcium sulfate lowered the initial decomposition temperature to 1000°C and desulfurization was complete in 1 hour at 1250°C. Hofman and Mostowitsch believed the reactions taking place to be these:

$$CaSO_4 + SiO_2 = CaSiO_3 + SO_2 + O \qquad (12)$$

$$2\ CaSO_4 + SiO_2 = Ca_2SiO_4 + 2\ SO_2 + O_2 \qquad (13)$$

Their results seemed to show that the rate of decomposition of calcium sulfate is proportional to the amount of silica present and the temperature employed. A mixture of ferric oxide and calcium sulfate began to decompose at 1100°C and the desulfurization was complete at 1250°C with complete fusion of the charge. The reaction presumed to take place was this:

$$CaSO_4 + Fe_2O_3 = CaO \cdot Fe_2O_3 + SO_2 + O \qquad (14)$$

Cobb (22) studied the decomposition of calcium sulfate alone and

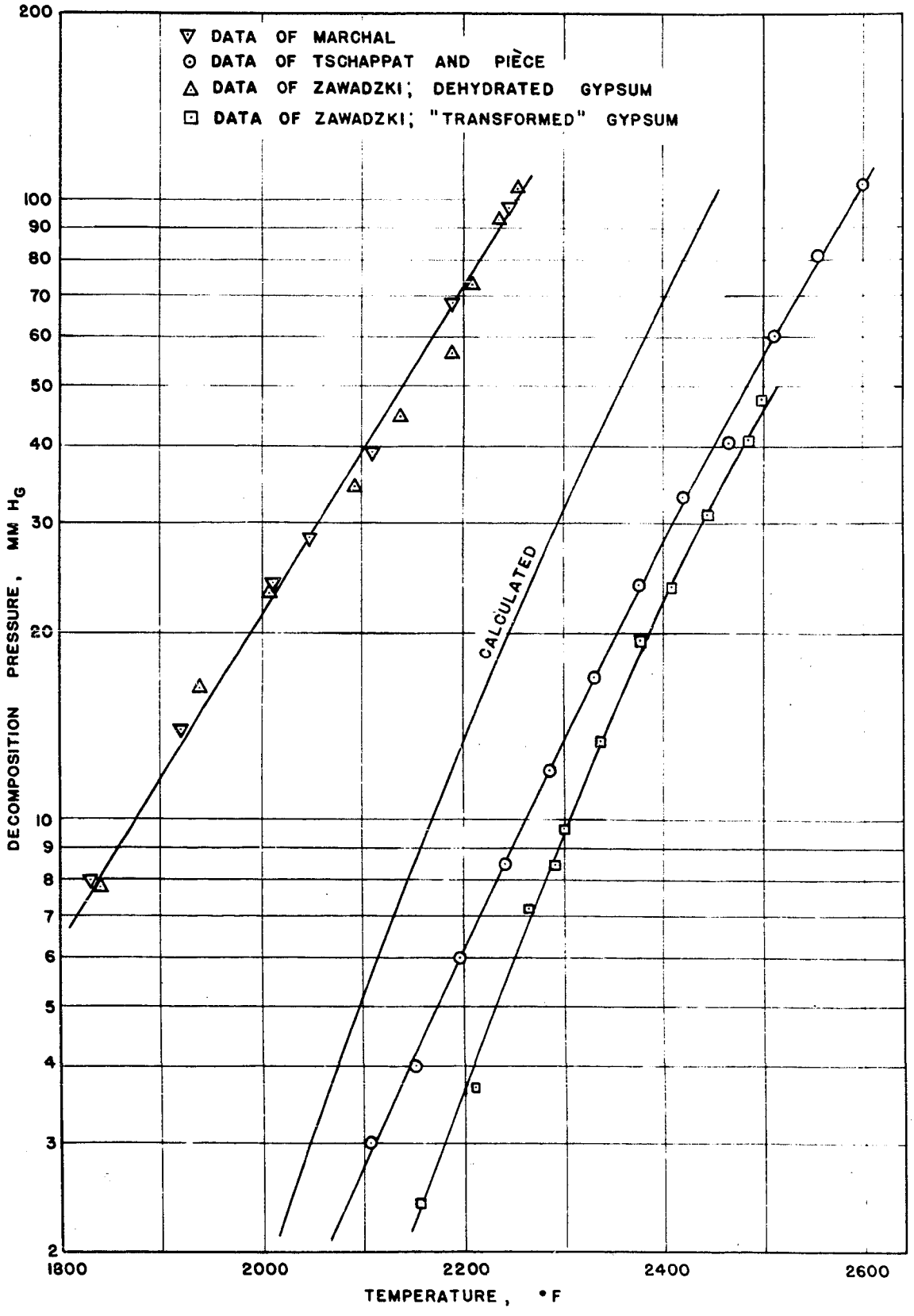
mixed with silica or alumina in both dry and moist air streams. In either atmosphere the initial dissociation temperature of pure calcium sulfate was in the range of 1225 to 1230°C. As the temperature was raised the decomposition rate increased very gradually and at 1380 to 1390°C a rapid evolution of sulfurous gases took place. When mixtures of calcium sulfate and silica in different proportions were heated in either dry or moist air, the initial decomposition temperature as determined by the evolution of sulfurous gases was always between 1005 and 1010°C. With alumina, calcium sulfate began to decompose at temperatures between 1120 and 1125°C.

When Budnikov and Syrkin (19) heated chemically pure gypsum in a stream of dry air, they observed decomposition to begin around 800°C. At 1375°C there was a sharp increase in the dissociation rate which seemed to indicate that the decomposition pressure had reached 1.0 atmosphere. Melting occurred simultaneously and decomposition was complete in 3 hours.

The equilibrium decomposition pressure at various temperatures between 1000 and 1230°C was determined for dehydrated chemically pure gypsum by Marchal (39). Her results are included in Figure 1. She also measured the decomposition pressures for dehydrated gypsum mixed with either silica, alumina, kaolin, or ferric oxide. Although alumina had a negligible effect, the dissociation pressure was increased significantly by ferric oxide, more by silica and most by kaolin.

The dissociation pressures of pure gypsum, anhydrite and specimens of naturally occurring gypsum from two quarries were determined at different temperatures by Terres (49). The values for pure gypsum and

Figure 1. Equilibrium decomposition pressure of calcium sulfate


DATA OF MARCHAL
DATA OF TSCHAPPAT AND PIÈCE
DATA OF ZAWADZKI; DEHYDRATED GYPSUM
DATA OF ZAWADZKI; "TRANSFORMED" GYPSUM
CALCULATED
DECOMPOSITION PRESSURE, MM H_G
TEMPERATURE, °F
200
100
90
80
70
60
50
40
30
20
10
9
8
7
6
5
4
3
2
1800
2000
2200
2400
2600

anhydrite almost coincided but they were much smaller than those observed by Marchal and corresponded more closely to those measured later by Tschäppät and Piece (50), also recorded in Figure 1. On the other hand, the decomposition pressures of the quarried samples were much larger and approached 1.0 atmosphere at about 1250°C. Terres attributed the greater dissociation pressures to the small percentage of impurities in the natural gypsum. Dissociation pressures of mixtures of pure gypsum and either silica, alumina or ferric oxide were found to increase with increasing proportions of the addition agents. Mixtures containing silica had the highest decomposition pressures, while those containing ferric oxide had the lowest. A mixture having gypsum, silica and alumina in the ratios needed for making cement had a decomposition pressure of 1.0 atmosphere at about 1250°C.

Zawadzki (58) also measured the equilibrium dissociation pressure of calcium sulfate. He obtained one set of values for dehydrated gypsum which agreed closely with those of Marchal. But when the calcium sulfate had stood for a time at a temperature of around 1200°C, the decomposition pressure fell to a much lower value which corresponded to that of natural anhydrite. As a consequence, a second set of values was obtained for the "transformed" gypsum. Both sets have been reproduced in Figure 1.

Bischoff (11) reported that passing a stream of water vapor over gypsum heated to 1200°C increased the rate of decomposition over that obtained with a stream of air. He also noted the effect of passing sulfur dioxide, oxygen, air, argon, nitrogen, moist air, and water vapor over an equimolar mixture of dehydrated gypsum and silica at 1100°C for 4 hours. The sample exposed to sulfur dioxide was only slightly desulfurized, the

samples exposed to oxygen or air were about 20 per cent desulfurized, those exposed to argon or nitrogen around 30 per cent desulfurized, and the samples exposed to water vapor over 90 per cent desulfurized. In the sample residues calcium oxide arising from the decomposition was found combined with silica. The latter was apparently effective in increasing the desulfurization rate. An increase in temperature in the range of 1050 to 1150°C had the effect of increasing the desulfurization rate of gypsum and silica mixtures in either air, nitrogen or water vapor atmospheres; the data seemed to fit the Arrhenius equation.

The previous work served to arouse the interest of Briner and Knodel (14) who proceeded to study the effect of water vapor on the dissociation of natural anhydrite and pure calcium sulfate. They found that pure calcium sulfate at 1300°C decomposed about five times as fast in a stream of water vapor as in a stream of air.

Briner et al. (13, 15) calculated the equilibrium dissociation pressures from thermodynamic data for calcium sulfate by itself and for calcium sulfate mixed with silica at 1300 and 1500°K. They subsequently measured the corresponding pressures experimentally and in addition determined the decomposition pressure of calcium sulfate mixed with metakaolin. Their calculated and measured values for pure calcium sulfate at 1500°K were in agreement and of the same magnitude as later determined by Tschäppät and Piece (50). But for the case of calcium sulfate mixed with silica the calculated and measured values were in great disagreement with each other and also with Marchal's measurements (39).

The effects of addition agents, water vapor, and reduced pressure in different combinations on the decomposition rate of pure calcium sulfate

were also studied by Briner et al. (16). They observed that all of the addition agents tested, which included silica, metakaolin, and three types of bauxite, increased the rate of desulfurization at 900°C. Water vapor, though, seemed to accelerate the decomposition more than any of the addition agents and was effective alone or in combination with the addition agents. When a mixture of water vapor and nitrogen was passed over heated calcium sulfate, some dissociation of the latter occurred even at temperatures as low as 600°C. Reducing the pressure to about 0.16 atmosphere in combination with addition agents and water vapor also increased the rate of decomposition.

Work conducted by the Tennessee Valley Authority on the desulfurization of phosphogypsum, which is a by-product in the manufacture of wet-process phosphoric acid, was reported by Stinson and Mumma (48). Preliminary tests which involved heating mixtures of phosphogypsum and silica in air both with and without the addition of carbon indicated that satisfactory desulfurization could be obtained below fusion temperatures without the use of carbon. When pellets containing phosphogypsum, silica, and iron and aluminum oxides were heated in a stream of air, the desulfurization rate was found to depend upon the composition, temperature, silica particle size, and pellet size.

Although many of the previous reports indicated that addition agents promoted the decomposition of calcium sulfate, West and Sutton (54) apparently found otherwise. They noted that differential thermal analysis curves for mixtures of gypsum and either silica, ferric oxide, aluminum hydroxide, or dialyzed kaolinite were the same as for gypsum alone. In none of the cases did there appear to be any reaction between

dissociation pressure of calcium sulfate was determined by the static method in the temperature range of 1425 to 1700°K. Reversibility of the following reaction was shown:

$$CaSO_4 = CaO + SO_2 + \tfrac{1}{2} O_2 \qquad (1)$$

Two samples of naturally occurring gypsum and one of anhydrite as well as a sample of chemically pure gypsum produced the same results. None of the samples contained significant amounts of silica or iron and aluminum oxides. The observed values agreed well with values calculated by the authors from thermodynamic data. For comparison the values measured by Tschäppät and Piece are plotted in Figure 1 with those of Marchal and Zawadzki.

Effect of Reducing Gases on Calcium Sulfate

Hofman and Mostowitsch (31) found that calcium sulfate was quantitatively reduced to calcium sulfide by carbon monoxide according to the following reaction:

$$CaSO_4 + 4\ CO = CaS + 4\ CO_2 \qquad (4)$$

At 700°C the reaction was barely perceptible but the rate increased rapidly with temperature up to 900°C which was the maximum temperature investigated.

The effect of passing both dry and moist hydrogen over heated calcium sulfate was investigated by Cobb (22). In both cases some reaction occurred at temperatures as low as 290 to 310°C, as indicated by the evo-

the addition agent and gypsum below the transition temperature of insoluble anhydrite to the high temperature form. After heating to 1250°C, which is above the inversion temperature, X-ray analysis of the sample residues revealed the presence of calcium orthosilicate and calcium ferrite. These compounds, of course, were only found in the samples which originally contained silica and ferric oxide respectively. The conclusion reached was that the addition agents had little effect on the temperature at which gypsum decomposes.

In his investigation into the thermal decomposition of natural gypsum and anhydrite at elevated temperatures, Bollen (12) used two methods. The first employed a bench scale shaft furnace in which natural gas was burned with an excess of air directly in the bed of gypsum particles. The second utilized a fluidized bed reactor in which small batches of gypsum or anhydrite particles were fluidized by a stream of hot flue gas resulting from the combustion of natural gas. The first method did not prove too successful because operating temperatures above that where fusion begins were required to get a practical rate of desulfurization. Melting of the charge caused the shaft furnace to plug. In the second method fairly rapid and almost complete desulfurization of gypsum was demonstrated with the fluidized bed reactor at elevated but less than fusion temperature when natural gas was burned with a stoichiometric amount of air. The rate of decomposition was slower when excess air was fed. It was not demonstrated, however, whether a gas could be produced sufficiently rich in sulfur dioxide to be used by a sulfuric acid plant.

The most recent work reported in regard to the decomposition of calcium sulfate is that of Tschäppät and Piece (50). The equilibrium

dissociation pressure of calcium sulfate was determined by the static method in the temperature range of 1425 to 1700°K. Reversibility of the following reaction was shown:

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lution of hydrogen sulfide and the presence of sulfide in the residue. As the temperature was increased the evolution of hydrogen sulfide seemed to increase very slowly until a temperature of 1000°C was reached, and then more rapidly.

Riesenfeld (45) studied the action of methane alone and of mixtures of methane and water vapor passed over heated gypsum. In the temperature range of 800 to 1000°C calcium sulfate seemed to be quantitatively reduced by dry methane according to the reaction:

$$CaSO_4 + CH_4 = CaS + CO_2 + 2\ H_2O \qquad (15)$$

At the lower temperature limit the reaction proceeded very slowly but the rate increased rapidly with temperature. Between 1100 and 1400°C other reactions apparently came into play, giving rise to the formation of some calcium oxide and free sulfur. At 1200°C and above the residue was found to contain some carbon from the decomposition of methane. The proportion of calcium oxide in the residue was increased both by increasing the temperature and by adding water vapor to the methane, the effect of water vapor increasing in proportion to the amount added. It was discovered that gypsum could be completely converted into calcium oxide and sulfur dioxide, given sufficient time, by using a large ratio of water vapor to methane and a reaction temperature of 1200°C or higher.

The reduction of calcium sulfate by hydrogen, carbon monoxide, and hydrogen sulfide was examined by Zawadzki et al. (57). With hydrogen the following reaction appeared quantitative between 600 and 800°C:

$$CaSO_4 + 4\ H_2 = CaS + 4\ H_2O \qquad (5)$$

Although the rate was slight at 600°C, it was rapidly accelerated by temperature. Beginning at 850°C the reduction was complicated by the appearance of side reactions which liberated some of the sulfur and left behind some calcium oxide. The conversion of calcium sulfate to calcium oxide increased with temperature and above 1050°C it predominated. At this temperature the sulfur in the off-gas was present as sulfur dioxide for the most part with some free sulfur also being present. Similar results were obtained with carbon monoxide. The reaction

$$CaSO_4 + 4\ CO = CaS + 4\ CO_2 \qquad (4)$$

started at about 680°C and was quantitative up to 800°C. The conversion of part of the calcium sulfate to calcium oxide and sulfur dioxide began at about 825°C and increased with temperature but not so rapidly as in the case of hydrogen. Reduction by means of hydrogen sulfide seemed to be equivalent to using a mixture of hydrogen and sulfur since hydrogen sulfide is considerably dissociated at high temperatures. In the temperature range of 600 to 1000°C calcium sulfate was reduced to calcium sulfide at a rate which increased with temperature. Some calcium oxide was formed at temperatures of 700°C and above, but the conversion increased only slightly with temperature. Diluting the hydrogen sulfide with nitrogen increased the proportions of both calcium oxide and sulfur dioxide formed.

A process for the production of quicklime and sulfur dioxide which consisted of heating calcium sulfate to temperatures in the range of 1150 to 1250°C in a reducing flame was patented by Fleck (25). At these temperatures it was indicated that there was little danger of forming

dead-burnt lime. It was suggested that the process be carried out in a rotary kiln fired with a suitable gas such as coal gas or producer gas and insufficient air to effect complete combustion. Fleck reported that the time required for completion of the reaction depended upon the temperature and size of calcium sulfate particles. Thus at 1150°C 1 inch pieces of anhydrite required 6 hours burning but at 1250°C only 4 hours, while finely ground anhydrite required only 3 hours at 1150°C.

Reference has already been made to Bollen's work (12) with a small scale fluidized bed reactor in which gypsum and anhydrite were heated by hot flue gas. When the flue gas was of a reducing nature, the initial rate of desulfurization was somewhat greater than for the case of a neutral flue gas but complete desulfurization was prevented by the formation of some calcium sulfide. The proportion of this contaminant increased as the flue gas was made more reducing, but increasing the temperature decreased the proportion of calcium sulfide. Under reducing conditions no fusion of particles was observed at temperatures as high as 2450°F, while with oxidizing conditions fusion would start around 2375°F.

Burwell (20, 21) has recently patented a process for the recovery of lime and hydrogen sulfide from gypsum which comprises passing a mixture of a hydrocarbon gas and steam through finely divided calcium sulfate at a temperature of about 890 to 1000°C. The results of some laboratory experiments are reported in which natural gas or hydrogen, both with and without steam, was passed over heated gypsum. When dry natural gas was passed over gypsum at 900°C, some hydrogen sulfide was liberated and the solid residue contained carbon and considerable calcium sulfide. The results with dry hydrogen were similar. When a large excess of water vapor was

mixed with either of these reducing gases, hydrogen sulfide was evolved and in time the gypsum was completely converted to calcium oxide. A temperature of only 650°C, was apparently used in the case of the hydrogen-steam mixture.

Oxidation of Calcium Sulfide

Since it has generally been found that desulfurization of gypsum with reducing gases is incomplete because of the formation of calcium sulfide, the possibilities for removing this contaminant will be reviewed. However in this regard only the high temperature reactions between calcium sulfide and either oxygen, calcium sulfate, or steam will be considered as these seem to offer the most promise.

The oxidation of calcium sulfide at elevated temperatures by dry air was investigated by Hofman and Mostowitsch (31) and later by Budnikov and Rivlin (18). These authors obtained essentially the same results. For temperatures between 800 and 1100°C the following two reactions seemed to take place simultaneously, with the first predominating:

$$CaS + 2\ O_2 = CaSO_4 \qquad (16)$$

$$CaS + 3/2\ O_2 = CaO + SO_2 \qquad (17)$$

As the temperature was increased the proportion of calcium sulfide converted to calcium oxide increased, but even at 1100°C only about 37 per cent of the sulfur was liberated as sulfur dioxide.

Bollen (12) partially desulfurized gypsum with a reducing flue gas in a fluidized bed reactor and subsequently subjected the solids, which con-

tained a large percentage of calcium sulfide, to an oxidizing roast. During the oxidation step the solids were treated with hot flue gas containing excess air in the fluidized bed reactor at temperatures in the range of 1000 to 1200°C. By this means it was possible to increase the desulfurization from 40 or 50 per cent to around 90 per cent.

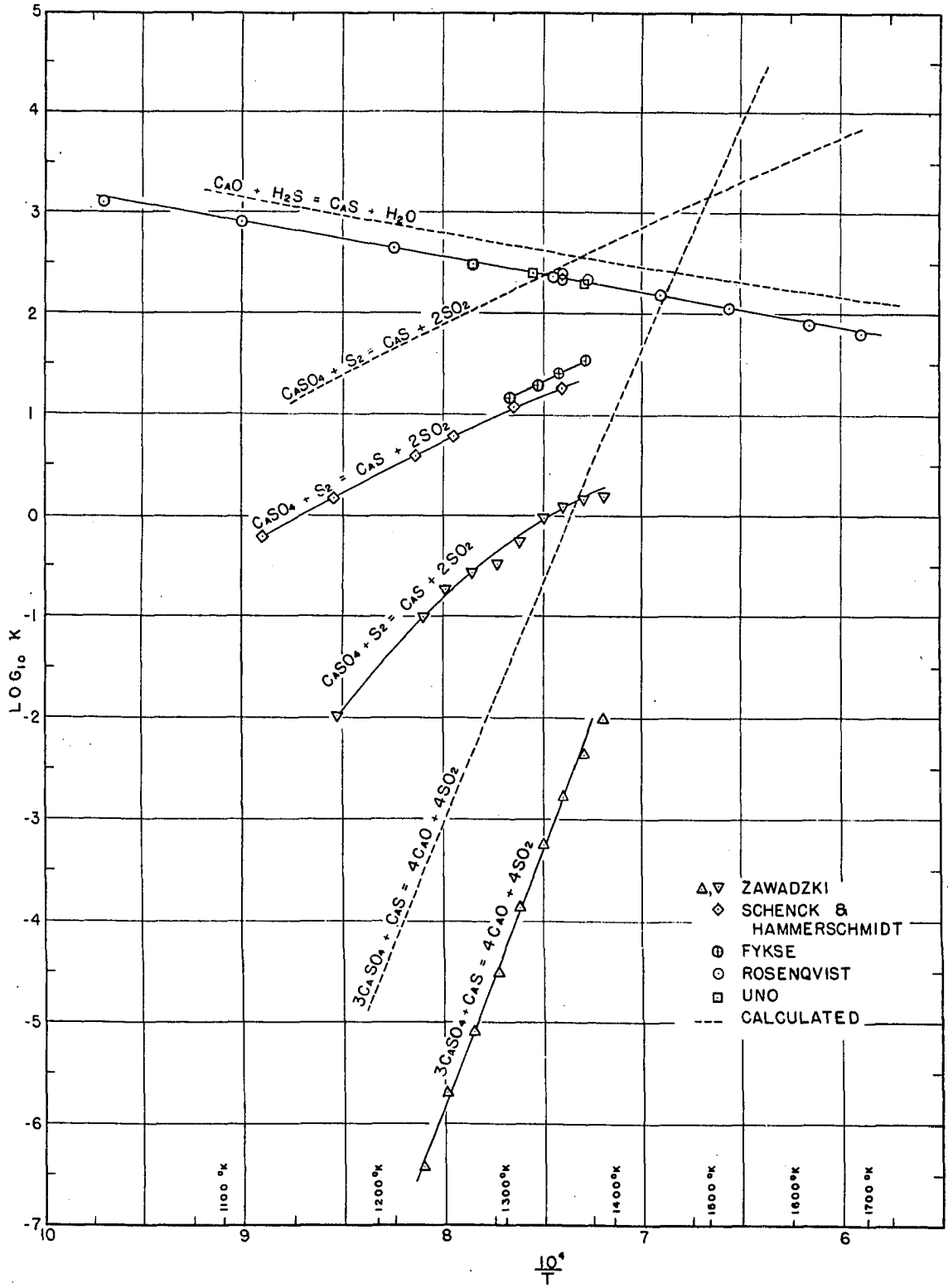
Several investigators have studied the following reaction between calcium sulfate and calcium sulfide:

$$CaS + 3\ CaSO_4 = 4\ CaO + 4\ SO_2 \qquad (7)$$

When Hofman and Mostowitsch (31) heated a mixture of the reactants to 1000°C in a stream of nitrogen, only about 29 per cent of the sulfur was freed. On the other hand, Neumann (42) obtained almost complete desulfurization under similar conditions. He found that if air were substituted for nitrogen the degree of desulfurization was lowered because of the oxidation of calcium sulfide to calcium sulfate. This was verified by Budnikov and Rivlin (18). The partial pressure of sulfur dioxide in equilibrium with a mixture of calcium sulfide and calcium sulfate was measured by Zawadzki (58) at different temperatures. The corresponding equilibrium constants are presented in Figure 2.

Riesenfeld (45) demonstrated that calcium sulfide could be desulfurized at temperatures in the range of 1000 to 1300°C by passing steam over it. Although the amount of steam needed for complete desulfurization decreased as the temperature increased, a very large excess was still required even at the highest temperature investigated. The sulfur in the off-gas was largely in the form of sulfur dioxide and free sulfur with a minor proportion of hydrogen sulfide.

Figure 2. Comparison of calculated and measured values of equilibrium constants


$CaO + H_2S = CaS + H_2O$
$CaSO_4 + S_2 = CaS + 2SO_2$
$CaSO_4 + S_2 = CaS + 2SO_2$
$CaSO_4 + S_2 = CaS + 2SO_2$
$3CaSO_4 + CaS = 4CaO + 4SO_2$
$3CaSO_4 + CaS = 4CaO + 4SO_2$
LOG$_{10}$ K
$\frac{10^4}{T}$
1100 °K
1200 °K
1300 °K
1400 °K
1500 °K
1600 °K
1700 °K
△,▽ ZAWADZKI
◇ SCHENCK & HAMMERSCHMIDT
⊕ FYKSE
⊙ ROSENQVIST
⊡ UNO
--- CALCULATED

The equilibrium of the following reaction between calcium sulfide and water vapor was determined by Rosenqvist (46):

$$CaS + H_2O = CaO + H_2S \qquad (6)$$

He employed the flow method whereby water vapor was passed through a heated mixture of calcium sulfide and calcium oxide. Hydrogen was added to the water vapor to prevent side reactions. Uno (51) checked the equilibrium of the reverse reaction by passing a mixture of hydrogen sulfide and hydrogen over heated calcium oxide. The equilibrium constants which were determined by these investigators are plotted in Figure 2. The values are such as to indicate that a process based on desulfurizing calcium sulfide with steam would be impractical.

REACTION EQUILIBRIA

Review of Principles

For the purpose of this investigation it was assumed that all the chemical reactions of interest were reversible reactions subject to the laws of chemical equilibrium. In a closed system with fixed temperature and pressure the decomposition of calcium sulfate according to the reaction

$$CaSO_{4(s)} = CaO_{(s)} + SO_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \qquad (1)$$

will proceed until a certain ratio of products to reactants is reached, whereupon no further reaction will occur. The final state of the system is known as the equilibrium state and it can be expressed mathematically as

$$K = \frac{(A_{CaO})(A_{SO_2})(A_{O_2})^{\frac{1}{2}}}{(A_{CaSO_4})} \qquad (18)$$

where K is the equilibrium constant and A_{CaO} is the activity of calcium oxide, etc. If the total pressure is 1.0 atmosphere, the activities of the gases may be taken as equal to their partial pressures and the activities of the solids may be taken as unity. Hence for this case the equilibrium expression reduces to

$$K_1 = P_{SO_2} P_{O_2}^{\frac{1}{2}} \qquad (19)$$

where P_{SO_2} and P_{O_2} are the partial pressures of sulfur dioxide and oxygen respectively.

It is apparent that the equilibrium constant itself is a measure of the tendency for the reaction to go to completion. The constant can either be determined experimentally or calculated from thermodynamic data. For most of the reactions considered the equilibrium constants were calculated by the method outlined below.

Method of Calculating Equilibrium Constants

Values for the reaction equilibrium constants were calculated by means of the expression

$$\log K = -\frac{1}{4.576}\left[\frac{\Delta H^\circ}{T} - \Delta S^\circ\right]_T \qquad (20)$$

where ΔH° is the standard enthalpy change and ΔS° the standard entropy change for the reaction and T is the absolute temperature. At 25°C values for the standard enthalpy change were obtained by adding and subtracting the appropriate standard heats of formation given by Perry (44, pp. 236-243). Values for the standard entropy change were obtained by adding and subtracting the appropriate absolute entropies given by Kelley (35). For higher temperatures the temperature corrections tabulated by Kelley (36) were applied in order to correct the standard enthalpy and entropy changes to the specified temperature.

Calculated Values of Equilibrium Constants

A number of chemical reactions were postulated for the system involving calcium sulfate and a reducing gas such as hydrogen or carbon

monoxide. Values of the logarithms of the equilibrium constants were calculated by the method outlined above for three different temperatures: 1200, 1400 and 1600°K. In addition the heats of reaction at 298, 1400 and 1600°K were also calculated. A list of the postulated reactions together with the calculated equilibrium values is presented in Table 1. A positive value of the logarithm of the equilibrium constant indicates that the corresponding reaction has a tendency to go toward the right while a negative value indicates a tendency for the reaction to go toward the left. The larger the value of the logarithm the more closely will the reaction approach completion when equilibrium is established. Also in Table 1, a positive value for the heat of reaction indicates that heat is absorbed by the reaction while a negative value indicates that heat is given off.

Calculated equilibrium constants for the reactions involving calcium compounds are shown graphically as a function of temperature in Figure 3 while the corresponding values for the reactions involving only gases are shown in Figure 4. If taken individually, most of the reactions would proceed toward the right and approach completion in a closed system for the range of temperature under consideration. Thus both reactions between calcium sulfate and carbon monoxide, if permitted to operate separately, would go to the point where the amounts of the reactants would be very small compared to the quantities of the products. On the other hand Reaction 1, illustrating the decomposition of calcium sulfate, should proceed only to a slight extent in the direction of decomposition.

The equilibrium for Reaction 7 is of special interest since the equilibrium expression is simply:

Table 1. Equilibrium constants and heats of reaction for postulated reactions

Text no.	Reaction	$\log_{10} K$ 1200°K (1700°F)	$\log_{10} K$ 1400°K (2060°F)	$\log_{10} K$ 1600°K (2420°F)	Heat of reaction, cal./g.mole 298°K (77°F)	Heat of reaction, cal./g.mole 1400°K (2060°F)	Heat of reaction, cal./g.mole 1600°K (2420°F)
1	$CaSO_{4(s)} = CaO_{(s)} + SO_{2(g)} + \frac{1}{2}O_{2(g)}$	-6.75	-3.93	-1.88	116,090	106,877	102,530
2	$CaSO_{4(s)} + CO_{(g)} = CaO_{(s)} + SO_{2(g)} + CO_{2(g)}$	0.98	2.06	2.78	48,454	39,753	35,784
3	$CaSO_{4(s)} + H_{2(g)} = CaO_{(s)} + SO_{2(g)} + H_2O_{(g)}$	1.14	2.42	3.32	58,292	47,154	42,544
4	$CaSO_{4(s)} + 4CO_{(g)} = CaS_{(s)} + 4CO_{2(g)}$	8.59	7.26	6.17	-46,114	-52,103	-54,687
5	$CaSO_{4(s)} + 4H_{2(g)} = CaS_{(s)} + 4H_2O_{(g)}$	9.24	8.71	8.32	-6,762	-22,499	-27,647
6	$CaO_{(s)} + H_2S_{(g)} = CaS_{(s)} + H_2O_{(g)}$	2.90	2.50	2.23	-15,628	-15,076	-14,864
7	$3CaSO_{4(s)} + CaS_{(s)} = 4CaO_{(s)} + 4SO_{2(g)}$	-4.67	0.96	4.95	239,930	211,115	197,823
21	$CaSO_{4(s)} + S_{2(g)} = CaS_{(s)} + 2SO_{2(g)}$	1.54	2.70	3.51	51,530	43,240	39,501
22	$CaO_{(s)} + 3/4S_{2(g)} = CaS_{(s)} + \frac{1}{2}SO_{2(g)}$	2.32	1.79	1.39	-21,335	-20,349	-19,830
23	$SO_{2(g)} + 2CO_{(g)} = 2CO_{2(g)} + \frac{1}{2}S_{2(g)}$	3.53	2.28	1.33	-48,822	-47,672	-47,094
24	$SO_{2(g)} + 2H_{2(g)} = 2H_2O_{(g)} + \frac{1}{2}S_{2(g)}$	3.84	2.99	2.39	-29,146	-32,870	-33,574
25	$SO_{2(g)} + 2H_2S_{(g)} = 2H_2O_{(g)} + 3/2S_{2(g)}$	1.15	1.43	1.67	11,454	10,545	9,932
26	$\frac{1}{2}S_{2(g)} + CO_{(g)} = COS_{(g)}$	0.02	-0.56	-1.00	-22,924	-22,017	-21,716
27	$\frac{1}{2}S_{2(g)} + H_{2(g)} = H_2S_{(g)}$	1.35	0.79	0.37	-20,280	-21,707	-21,753
28	$CO_{(g)} + H_2O_{(g)} = CO_{2(g)} + H_{2(g)}$	-0.16	-0.36	-0.54	-9,838	-7,401	-6,760

Figure 3. Equilibrium constants for reactions of calcium compounds

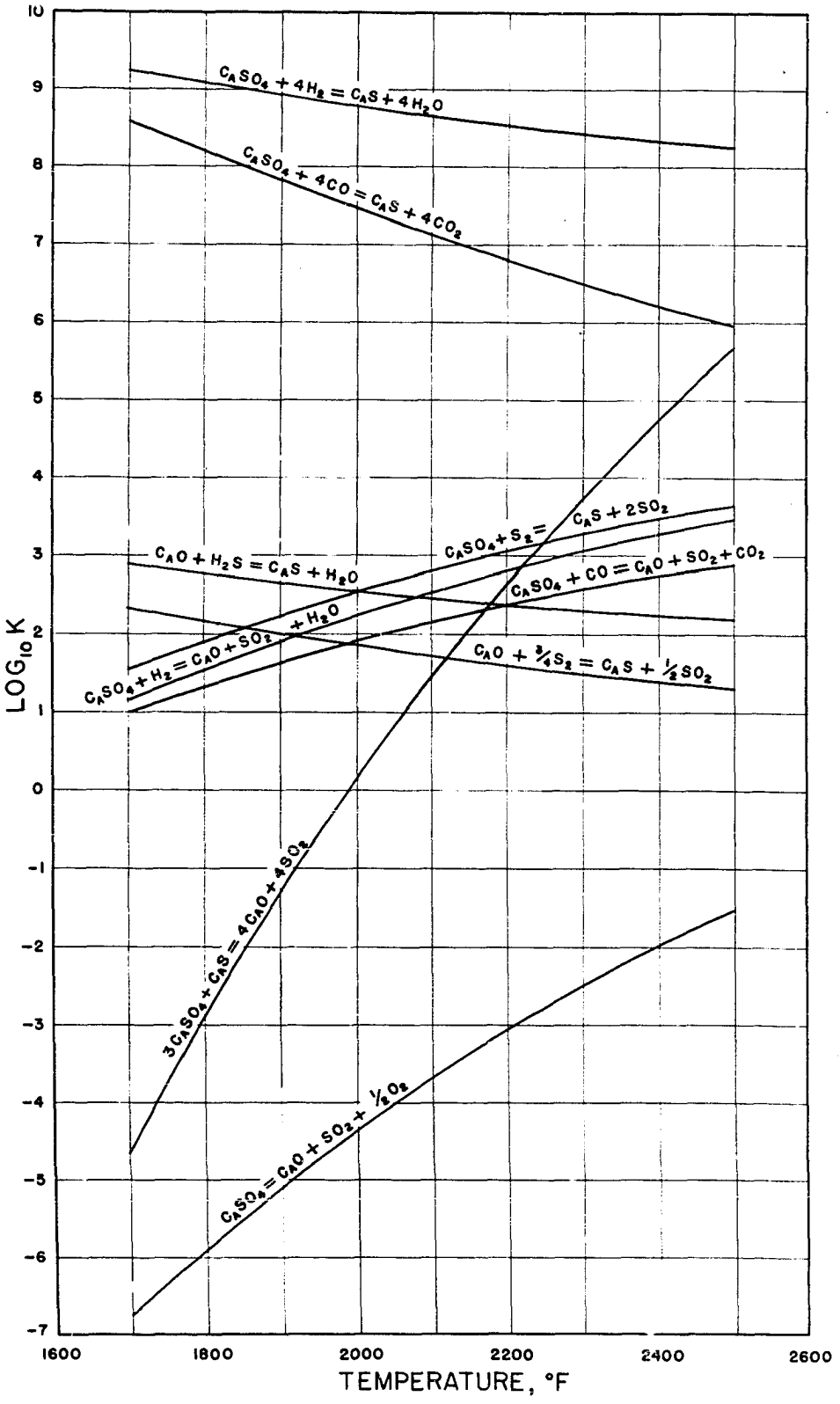
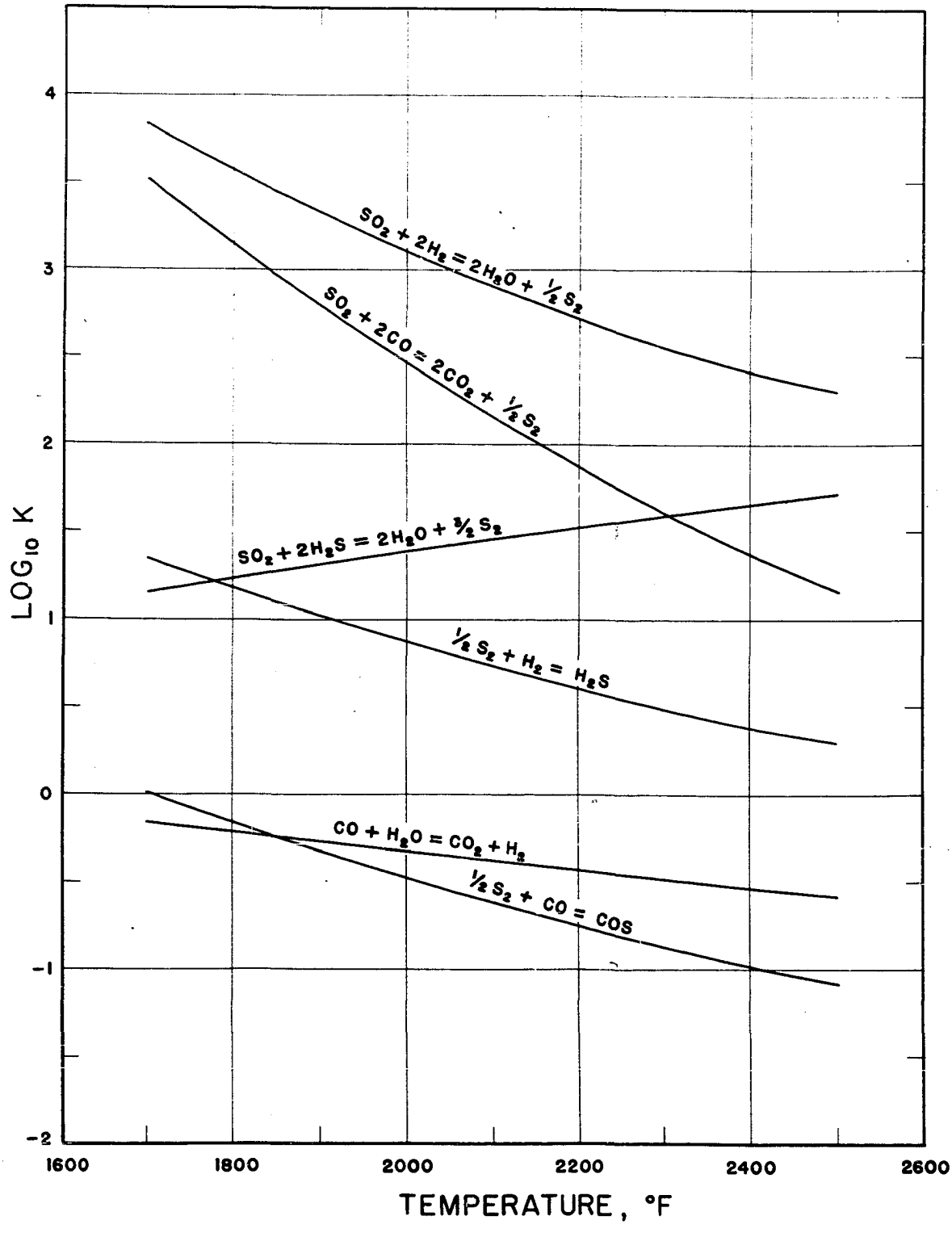

$C_ASO_4 + 4H_2 = C_AS + 4H_2O$
$C_ASO_4 + 4CO = C_AS + 4CO_2$
$C_AO + H_2S = C_AS + H_2O$
$C_ASO_4 + S_2 = C_AS + 2SO_2$
$C_ASO_4 + CO = C_AO + SO_2 + CO_2$
$C_ASO_4 + H_2 = C_AO + SO_2 + H_2O$
$C_AO + \frac{3}{4}S_2 = C_AS + \frac{1}{2}SO_2$
$3C_ASO_4 + C_AS = 4C_AO + 4SO_2$
$C_ASO_4 = C_AO + SO_2 + \frac{1}{2}O_2$
$LOG_{10}\ K$
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
1600
1800
2000
2200
2400
2600
TEMPERATURE, °F

Figure 4. Equilibrium constants for reactions of gaseous compounds


4
3
2
1
0
-1
-2
LOG10 K
1600
1800
2000
2200
2400
2600
TEMPERATURE, °F
SO2 + 2H2 = 2H2O + 1/2 S2
SO2 + 2CO = 2CO2 + 1/2 S2
SO2 + 2H2S = 2H2O + 3/2 S2
1/2 S2 + H2 = H2S
CO + H2O = CO2 + H2
1/2 S2 + CO = COS

$$K_7 = P_{SO_2}^4 \qquad (29)$$

Consequently the partial pressure of sulfur dioxide in equilibrium with a mixture of calcium sulfate and calcium sulfide should be a function of the temperature only. The partial pressure should reach a value of 1.0 atmosphere at a temperature of 1990°F. If a mixture of the reactants is heated under atmospheric pressure above this temperature in a closed system, the reaction should proceed until one or both of the reactants is used up. In other words, calcium sulfate and calcium sulfide cannot be in equilibrium with each other above this temperature without increasing the partial pressure of sulfur dioxide above 1.0 atmosphere.

By considering the equilibrium constants for the hypothesized reactions it is possible to estimate the principal products which would be formed if calcium sulfate and a reducing gas such as carbon monoxide were brought together in a closed system and equilibrium were approached under atmospheric pressure and a temperature of say 2200°F. If carbon monoxide and calcium sulfate were mixed in a ratio of 1.0, Reaction 2 should control the equilibrium and hence the reactants should be almost entirely converted into calcium oxide, sulfur dioxide and water vapor. Conversion of part of the calcium sulfate into calcium sulfide should not occur because any sulfide formed would have to react with the remaining sulfate according to Reaction 7 before equilibrium was established. If the initial ratio of carbon monoxide to calcium sulfate were between 1.0 and 4.0, a solid product containing both calcium oxide and calcium sulfide would be expected. In this case 1.0 mole of carbon monoxide per mole of calcium sulfate might still be used to convert the sulfate into the oxide

by Reaction 2. The excess carbon monoxide, however, would then be able to reduce part of the sulfur dioxide to sulfur by Reaction 23 and the sulfur in turn could react with part of the calcium oxide to form some calcium sulfide. The series of reactions is summarized below:

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad (2)$$

$$SO_2 + 2\ CO = 2\ CO_2 + \tfrac{1}{2}\ S_2 \qquad (23)$$

$$CaO + \tfrac{3}{4}\ S_2 = CaS + \tfrac{1}{2}\ SO_2 \qquad (22)$$

These three reactions can be combined to form Reaction 4 so the net result would be the same as if Reactions 2 and 4 took place simultaneously:

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad (2)$$

$$CaSO_4 + 4\ CO = CaS + 4\ CO_2 \qquad (4)$$

If the initial ratio of carbon monoxide to calcium sulfate were equal to 4.0, then Reaction 4 should control the equilibrium and the calcium sulfate should be completely converted into calcium sulfide.

A similar line of reasoning can be used for a system involving calcium sulfate and hydrogen because the calculated equilibrium constants are of the same order of magnitude for the corresponding reactions.

Measured Equilibrium Data

Equilibrium data for several of the reactions postulated in the previous section have been determined experimentally at elevated temperatures by other investigators. These experimental values provide a means for checking the equilibrium constants calculated in this work.

Consider Reaction 1. The decomposition pressure of calcium sulfate may be defined as the sum of the partial pressures of sulfur dioxide and oxygen at equilibrium. From the stoichiometry it follows that the decomposition pressure can be expressed as a function of the equilibrium constant.

$$P = P_{SO_2} + P_{O_2} = 1.89\, K_1^{2/3} \qquad (30)$$

For comparison, values of the decomposition pressure obtained from the calculated constants are plotted as a function of temperature in Figure 1 along with experimentally determined values found in the literature. The upper curve on this graph represents the earlier measurements made separately by Marchal (39) and Zawadzki (58) for dehydrated gypsum. Later Zawadzki observed that if the material were held at a temperature of around 1200°C or above for a period of several hours, the decomposition pressure gradually fell to a much lower but constant value which seemingly corresponded with the value obtained for a sample of natural anhydrite. He subsequently regarded the larger decomposition pressures as not true equilibrium pressures and made a new set of measurements for the stabilized or "transformed" gypsum which correspond to the lower curve on the graph. Then Tschäppät and Piece (50) obtained values of the same order of magnitude using samples of natural anhydrite and both chemically pure and natural gypsum. They apparently did not observe the higher but transitory decomposition pressures. For the range of temperature involved the calculated values do not correspond closely with any of the experimental values.

Zawadzki (58) also obtained equilibrium data for both Reactions 7 and 21. The last reaction was subsequently investigated by Schenck and

Hammerschmidt (47) and Fykse (27). Equilibrium constants based on these experimental studies are plotted as a function of temperature in Figure 2 together with calculated values. For neither of these reactions do the calculated values agree well with the experimental values. In the case of Reaction 21 the values found by Fykse compare closely with those of Schenck and Hammerschmidt, but neither agree with those of Zawadzki.

Reaction 6 was studied separately by both Rosenqvist (46) and Uno (51) and their results were in agreement. The equilibrium constants based on these two works are plotted in Figure 2 with the calculated values for comparison. For this reaction the calculated and experimental values seemed to be in fair agreement.

The relatively large differences noted between the calculated and experimental values for Reactions 1, 7 and 21 may have been due to inaccuracies in the thermodynamic properties on which the calculated equilibrium constants were based. Since thermodynamic properties of gases are generally known more accurately than for solids at high temperatures and since calcium sulfate is the only solid component common to all three reactions, it is suspected that an error in the properties of calcium sulfate may be responsible. Then too, the structure of calcium sulfate changes as the temperature is increased. If the rate of transition is slow under some conditions, it may be that all of the investigators were not working with the same form of calcium sulfate. This seems to be the most logical explanation for the widely divergent decomposition pressures reported for gypsum.

Equilibrium Conversion

To determine the thermodynamic feasibility of an industrial process based on the attainment of equilibrium in the system formed by bringing together gypsum and a reducing gas, the equilibrium conversions of calcium sulfate to calcium oxide and to calcium sulfide were calculated for various conditions. The problem was essentially one of determining the amount of each component present at equilibrium for a given temperature and pressure and specified quantities of starting materials. Two reducing gases were considered, carbon monoxide and hydrogen. They were treated separately in order to simplify the calculations.

Using carbon monoxide

When carbon monoxide and calcium sulfate are brought together in a closed system, it is possible to have several components present in both the solid and gas phases at equilibrium. For a pressure of 1.0 atmosphere and for the relevant temperature range, the following components might be present in significant amounts:

Gases	Solids
CO	$CaSO_4$
CO_2	CaO
S_2	CaS
SO_2	

Not included is carbon oxysulfide since it would be largely dissociated at the temperatures of interest. Furthermore, because of the relatively high temperatures, calcium sulfate and calcium sulfide could not both be

present at equilibrium. Hence, for an initial ratio of carbon monoxide to calcium sulfate greater than 1.0, the components present at equilibrium should consist of calcium oxide and calcium sulfide and the four gases, but for a smaller ratio of reactants fewer components should be present. Thus, for an initial ratio of carbon monoxide to calcium sulfate less than 1.0, only calcium sulfate, calcium oxide, carbon monoxide, carbon dioxide, and sulfur dioxide should be present.

For the last case the system includes five components so there are five unknown quantities to calculate and five independent equations are needed for a solution of the conversion problem. Since there are four elements involved, four material balances can be made, one for each element. The equilibrium relationship shown below for Reaction 2 furnishes a fifth equation.

$$K_2 = \frac{P_{SO_2} P_{CO_2}}{P_{CO}} \tag{31}$$

For the case where a larger ratio of carbon monoxide to calcium sulfate is used six components and four elements are involved so it is necessary to make use of two independent equilibrium relationships. The following expressions corresponding to Reactions 22 and 23 are suitable since they are independent and involve all the components:

$$K_{22} = \frac{P_{SO_2}^{\frac{1}{2}}}{P_{S_2}^{3/4}} \tag{32}$$

$$K_{23} = \frac{P_{CO_2}^{2} P_{S_2}^{\frac{1}{2}}}{P_{CO}^{2} P_{SO_2}} \qquad (33)$$

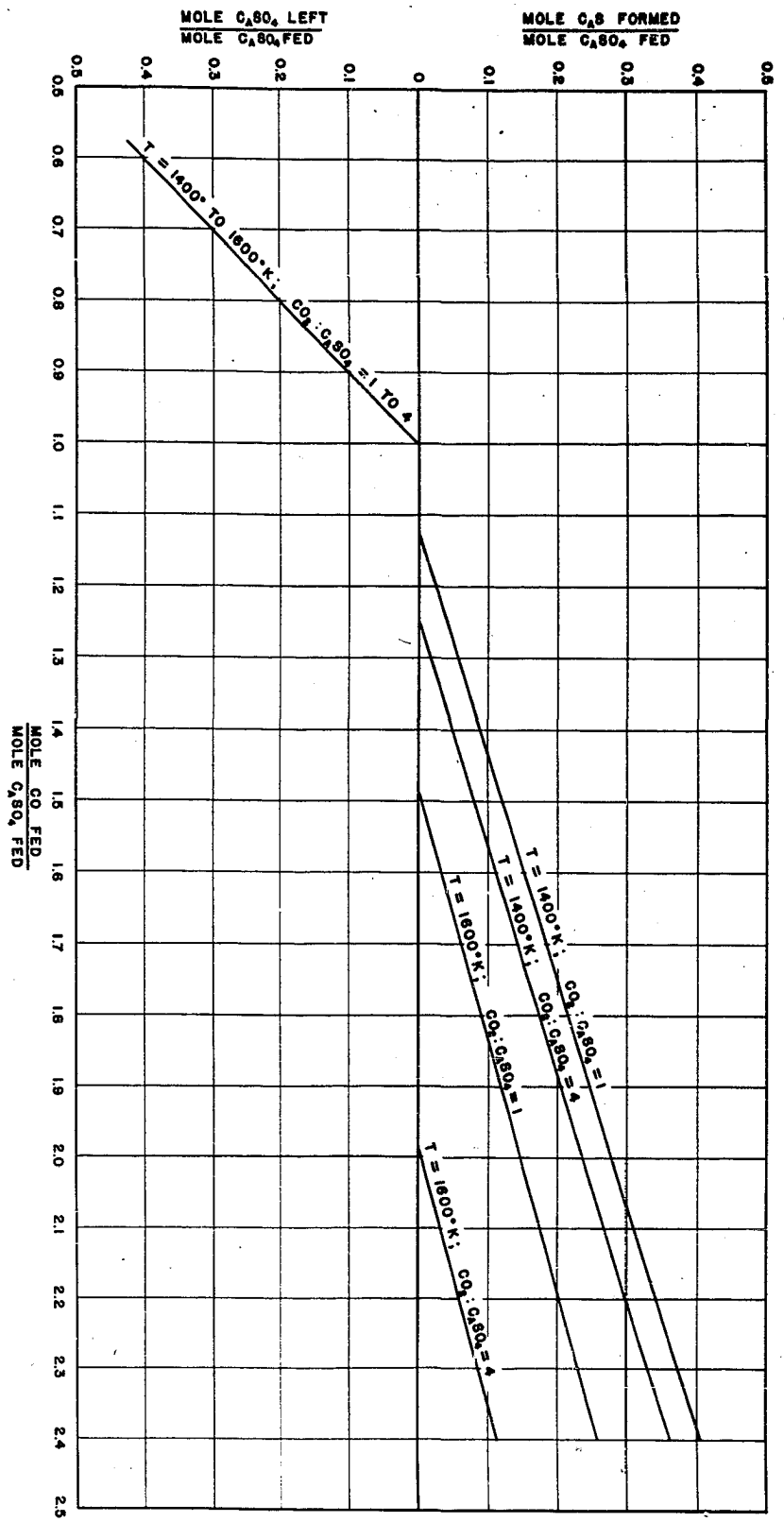
The problem then becomes one of multiple reaction equilibria.

In a foreseeable process a mixture of carbon monoxide, carbon dioxide, and nitrogen would probably be brought into contact with gypsum, rather than carbon monoxide alone. The initial ratios of carbon monoxide to calcium sulfate and of carbon dioxide to calcium sulfate would affect conversion as would also the temperature. On the other hand, the amount of nitrogen introduced in the beginning would not affect the conversion but it would affect the final concentrations.

By using the methods outlined above the equilibrium conversion was calculated for different ratios of carbon monoxide to calcium sulfate at two levels of temperature and at two levels of the ratio of carbon dioxide to calcium sulfate. The temperatures selected were 1400 and 1600°K, and the ratios of carbon dioxide to calcium sulfate chosen were 1.0 and 4.0. Calculated values of the equilibrium constants were used in determining the conversion. The results are summarized in the conversion chart, Figure 5.

The conversion chart is divided into two parts; the upper half representing the region in which calcium oxide and calcium sulfide are present in the solid phase, the lower half representing the region in which calcium sulfate and calcium oxide are present. Thus the ordinates in the upper half of the chart represent the proportion of calcium sulfate converted into calcium sulfide while the ordinates in the lower half represent the

Figure 5. Equilibrium conversion using carbon monoxide


MOLE C_4S0_4 LEFT / MOLE C_4S0_4 FED
MOLE C_4S FORMED / MOLE C_4S0_4 FED
MOLE CO FED / MOLE C_4S0_4 FED
T = 1400° TO 1600°K; $CO_2 : C_4S0_4$ = 1 TO 4
T = 1400°K; $CO_2 : C_4S0_4$ = 1
T = 1400°K; $CO_2 : C_4S0_4$ = 4
T = 1600°K; $CO_2 : C_4S0_4$ = 1
T = 1600°K; $CO_2 : C_4S0_4$ = 4

proportion of calcium sulfate remaining unconverted into calcium oxide. The zero ordinate or the line dividing the two parts represents complete conversion to calcium oxide.

For a carbon monoxide to calcium sulfate feed ratio less than 1.0 and for the selected range of conditions, the conversion is independent of temperature and of the amount of carbon dioxide fed. This is not true for a feed ratio larger than 1.0.

The points of intersection of the slanted lines with the zero ordinate are of most interest since they represent sets of conditions which would result in complete desulfurization of the calcium sulfate. A comparison of these conditions shows that as the temperature and proportion of carbon dioxide increase the feed ratio of carbon monoxide to calcium sulfate becomes less critical. For example, at 1600°K and an initial carbon dioxide to calcium sulfate ratio of 4.0, complete conversion to the oxide should be obtained for any feed ratio between 1.0 and 2.0. At 1400°K the range is much smaller.

Equilibrium gas compositions were determined for the sets of conditions known to provide complete desulfurization. For this purpose 10 moles of feed gas containing carbon monoxide, carbon dioxide, and nitrogen were assumed to be introduced with each mole of calcium sulfate. This ratio of feed gas to calcium sulfate approximates a value which might be used in practice. The assumed feed gas compositions and the corresponding equilibrium compositions are listed in Table 2. In every case the equilibrium concentration of sulfur dioxide was about 9 per cent and in no case was the concentration of sulfur vapor more than a fraction of a per cent. These concentrations are relative, for an increase or decrease in the proportion

Table 2. Equilibrium gas compositions for 100% desulfurization of calcium sulfate by means of carbon monoxide

(moles feed gas / moles $CaSO_4$ = 10)

Temp. °K	Gas composition, mole %			
	Feed		Equilibrium	
1400	CO	10.00	CO	0.01
	CO_2	10.00	CO_2	18.17
	N_2	80.00	N_2	72.74
		100.00	SO_2	9.08
				100.00
1400	CO	11.25	CO	0.76
	CO_2	10.00	CO_2	18.58
	N_2	78.75	N_2	71.66
		100.00	SO_2	8.92
			S_2	0.08
				100.00
1400	CO	12.48	CO	1.88
	CO_2	40.00	CO_2	45.88
	N_2	47.52	N_2	43.24
		100.00	SO_2	8.92
			S_2	0.08
				100.00
1600	CO	14.82	CO	3.27
	CO_2	10.00	CO_2	19.36
	N_2	75.18	N_2	68.54
		100.00	SO_2	8.56
			S_2	0.27
				100.00
1600	CO	19.84	CO	7.88
	CO_2	40.00	CO_2	46.68
	N_2	40.16	N_2	36.61
		100.00	SO_2	8.56
			S_2	0.27
				100.00

of nitrogen in the feed gas would result in a corresponding change in the equilibrium concentrations.

The results of these calculations show that a range of conditions exists under which the attainment of equilibrium would provide complete desulfurization of gypsum and simultaneous production of sulfur dioxide.

Using hydrogen

An equilibrium conversion chart was also prepared for the system involving hydrogen and calcium sulfate. The general method of calculation was the same as before; however, the components were different. Hydrogen and water vapor replaced carbon monoxide and carbon dioxide respectively. Hydrogen sulfide was an additional component to be considered and the number of simultaneous equations was increased by one. Figure 6 is the resulting conversion chart. For a hydrogen to calcium sulfate feed ratio of 1.0 or less the conversion is exactly the same as for the previous system, but for higher feed ratios both temperature and the initial ratio of water vapor to calcium sulfate have less influence than do the corresponding conditions in the previous system.

The equilibrium gas compositions for several sets of conditions which would result in complete conversion of calcium sulfate to calcium oxide are listed in Table 3. The sulfur dioxide concentration varies from 8.3 to 9.1 per cent and the concentrations of sulfur vapor and hydrogen sulfide are never more than a fraction of a per cent.

It is apparent from these studies that an equilibrium process involving calcium sulfate and either carbon monoxide or hydrogen is thermodynamically feasible under the conditions specified in the conversion charts.

Figure 6. Equilibrium conversion using hydrogen

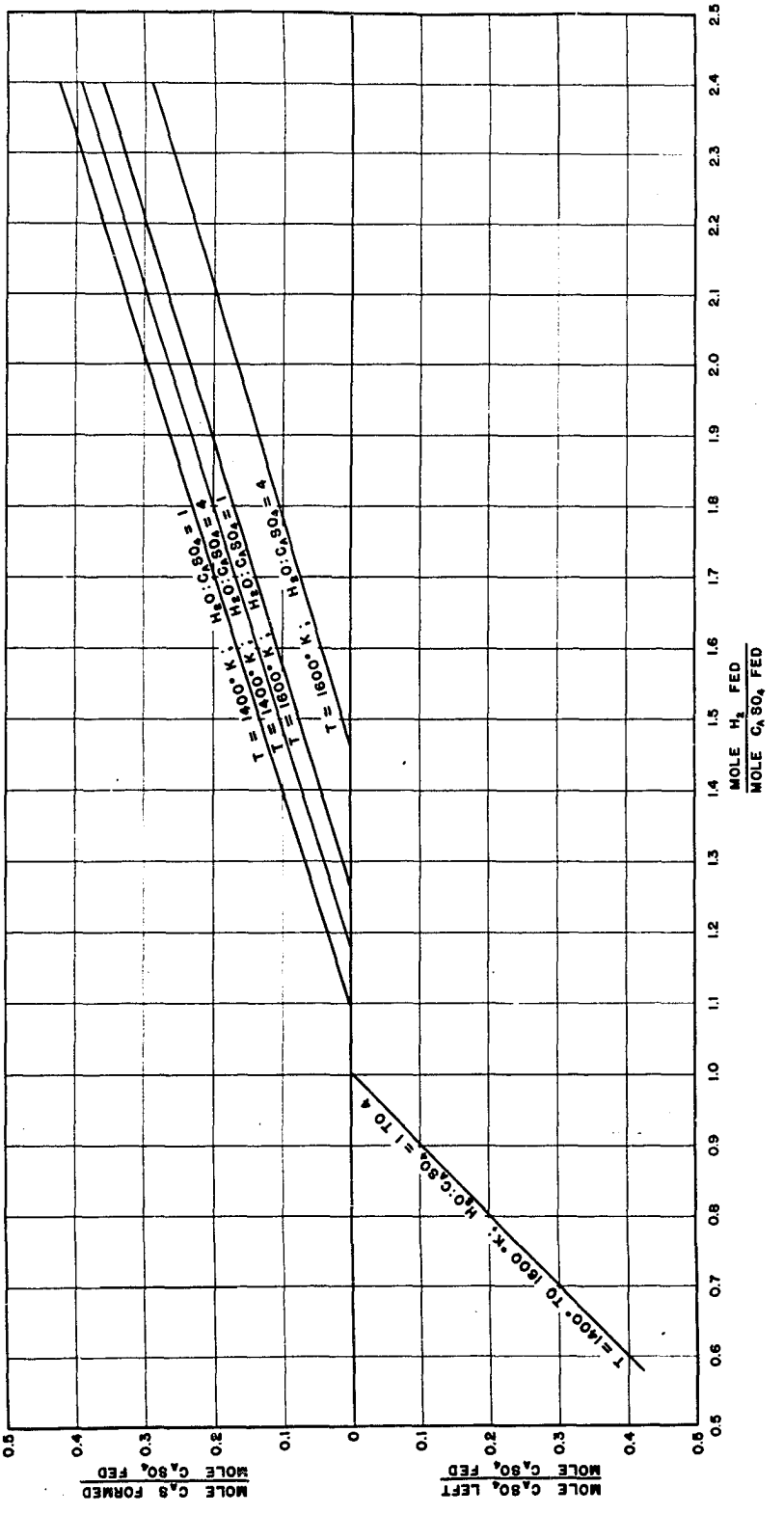

T = 1400° K.; H2O:CaSO4 = 1
T = 1400° K.; H2O:CaSO4 = 4
T = 1600° K.; H2O:CaSO4 = 1
T = 1600° K.; H2O:CaSO4 = 4
T = 1400° TO 1600° K.; H2O:CaSO4 = 1 TO 4
MOLE CaSO4 FORMED / MOLE CaSO4 FED
MOLE CaSO4 LEFT / MOLE CaSO4 FED
MOLE H2 FED / MOLE CaSO4 FED

Table 3. Equilibrium gas compositions for 100% desulfurization of calcium sulfate by means of hydrogen

(moles feed gas / moles $CaSO_4$ = 10)

Temp. °K	Gas composition, mole % Feed		Equilibrium	
1400	H_2	10.00	H_2	0.01
	H_2O	10.00	H_2O	18.18
	N_2	80.00	N_2	72.72
		100.00	SO_2	9.09
				100.00
1400	H_2	10.00	H_2	0.02
	H_2O	40.00	H_2O	45.45
	N_2	50.00	N_2	45.45
		100.00	SO_2	9.08
				100.00
1600	H_2	10.00	H_2	(trace)
	H_2O	10.00	H_2O	18.18
	N_2	80.00	N_2	72.73
		100.00	SO_2	9.09
				100.00
1400	H_2	10.94	H_2	0.34
	H_2O	10.00	H_2O	19.07
	N_2	79.06	N_2	71.98
		100.00	SO_2	8.88
			S_2	0.08
			H_2O	0.06
				100.41
1400	H_2	11.78	H_2	0.85
	H_2O	40.00	H_2O	46.61
	N_2	48.22	N_2	43.94
		100.00	SO_2	8.80
			S_2	0.08
			H_2S	0.15
				100.43
1600	H_2	12.60	H_2	0.96
	H_2O	10.00	H_2O	19.42
	N_2	77.40	N_2	70.63
		100.00	SO_2	8.48
			S_2	0.26
			H_2S	0.11
				99.86
1600	H_2	14.60	H_2	2.36
	H_2O	40.00	H_2O	47.50
	N_2	45.40	N_2	41.49
		100.00	SO_2	8.35
			S_2	0.26
			H_2S	0.28
				100.24

Process Applications

The possibility of utilizing Reaction 1 for the decomposition of gypsum in an industrial process is not definite from the available equilibrium data. In order to cause the reaction to go to completion it would be necessary to keep the partial pressures of sulfur dioxide and oxygen below their equilibrium partial pressures. This might be accomplished by passing an inert gas over the heated gypsum to sweep away the gaseous decomposition products. The maximum concentration of sulfur dioxide in the off-gas from such a process would be limited by the equilibrium partial pressure. Since the off-gas would have to have several per cent sulfur dioxide to be used for the manufacture of sulfuric acid, the equilibrium partial pressure is a determining factor. There is, however, too much disagreement among the values of the decomposition pressure for calcium sulfate observed by other investigators to establish definitely the equilibrium partial pressures. If the higher decomposition pressures observed by both Marchal (39) and Zawadzki (58) (Figure 1) were realized, the maximum possible concentration of sulfur dioxide in the off-gas from the hypothetical process could be 10 per cent at a temperature of 2300°F. But if the decomposition pressures observed by Tschappat and Piece (50) hold, then the off-gas could contain a maximum of only 1 per cent sulfur dioxide at a temperature of 2300°F and only 2.5 per cent at 2400°F. The lower decomposition pressures measured by Zawadzki for "transformed" gypsum would result in a still lower concentration of sulfur dioxide. It seems fairly obvious then that Reaction 1 could only serve as a basis for an industrial process providing the larger values of Marchal and Zawadzki hold.

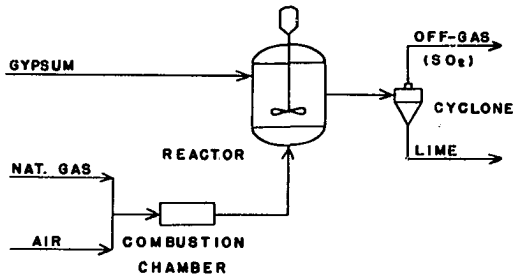
The equilibrium conversion charts (Figures 5 and 6) indicate the possibilities for using equilibrium in a system of gypsum and reducing gases as the basis for an industrial process. Whether the process is economical or not will depend to a large extent on the reaction kinetics. If the essential reactions proceed rapidly, the time required to approach the equilibrium state will be short and relatively small equipment will be needed for a given production rate. Conversely if the reactions are slow, the size of the equipment may be prohibitively large.

There are several ways in which an industrial process might be carried out. One possible process is illustrated in Figure 7a. In this process powdered gypsum and a hot reducing gas resulting from the combustion of natural gas with a limited supply of air would be fed simultaneously to a stirred tank reactor. The latter would mix the reactants completely and provide sufficient residence time for equilibrium to be approached. The product mixture would be withdrawn continuously and separated into solid and gaseous fractions. This process is based on continuous rather than batchwise operation because economic considerations would normally be expected to indicate this choice. Needless to say, there would be great difficulties connected with this process regardless of the equilibrium and kinetic aspects. For example, it would be highly problematical whether a mechanical agitator could be developed which would suspend the solids in the gas and withstand the extreme service conditions.

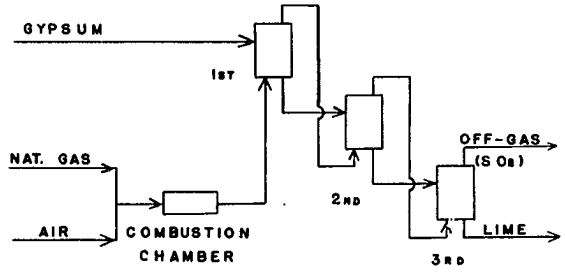
A more realistic processing method might utilize a fluidized bed reactor which provides good mixing between gases and solids by employing large enough gas flow rates to keep the solids in suspension without need for mechanical agitation. In such a reactor the solids might be sufficiently

Figure 7. Various types of equilibrium reactors

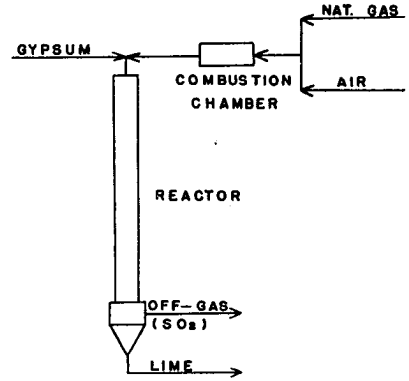
a. Stirred tank reactor
b. Fluidized bed reactors
c. Moving bed reactor



(A) STIRRED TANK REACTOR



(B) THREE STAGE FLUIDIZED SOLIDS REACTOR



(C) MOVING BED REACTOR

agitated so that a sample of them taken from one part of the reactor would not vary much in composition from a sample taken from another part. However, backmixing of the gas stream would probably be limited so that the gas composition would be expected to vary between the top and bottom of the reaction vessel. An equilibrium process would be attained if the gases leaving the reactor were in equilibrium with the solids. Perhaps a single stage would not provide the necessary contact. In that case several stages in series with cocurrent flow between them could be used. Such a process is illustrated by Figure 7b. Crushed and sized gypsum and a hot reducing gas would be fed continuously to the first stage. After the first contact the phases would be separated and introduced separately to the second stage and so on. Equilibrium would be approached in the last stage and a final separation of the phases would give the two product streams.

Another process which might be used industrially is a moving bed process such as shown in Figure 7c. Relatively large lumps of gypsum and a hot reducing gas would be fed continuously to the top of a refractory lined shaft which would be filled with a slowly moving bed of solids. The gas and solids would descend cocurrently but at different velocities. By making the shaft tall enough equilibrium would be approached at the bottom of the shaft and separation of the phases would yield the two products.

If it developed that the reactions are exceedingly rapid, then still another process might be used. This one could be called a falling particle process. The flowsheet would be similar to Figure 7c but instead of large lumps, very fine particles of gypsum would be used and these would be allowed to fall freely through the shaft. The gas and solids would move

downward together at roughly the same velocity and equilibrium would have to be attained in the short time interval taken by the particles to fall to the bottom of the shaft.

In the shaft furnace process which was selected for investigation on a pilot plant scale the stream of hot reducing gases flows upward and countercurrent to the descending bed of solids. Consequently it does not provide for the attainment of equilibrium and instead probably increases the driving force for some reactions. Whether or not the desired reactions are favored remains to be seen.

LABORATORY INVESTIGATION

The study of the thermodynamic equilibria showed that reductive decomposition would probably be feasible, while that of thermal decomposition would be questionable. Calcium sulfate apparently has two different decomposition pressures at high temperature. If the higher decomposition pressure could be realized and the rate was not limiting, thermal decomposition could yield an off-gas containing 9 per cent sulfur dioxide at 2250°F and 10 per cent at 2300°F. These concentrations fall in the range normally used for sulfuric acid manufacture. According to Barr (9) the optimum content of sulfur dioxide for gas fed to acid plants is about 7 per cent while plants can be designed to operate efficiently on gas containing as little as 3 per cent sulfur dioxide.

In the laboratory, the feasibility of thermal decomposition was investigated by passing a mixture of sulfur dioxide and oxygen (the decomposition products), diluted with an inert gas, over gypsum heated to a temperature in the range of 2200 to 2300°F. It was postulated that if the gypsum decomposed at a reasonable rate when the gas being fed contained 3 to 7 per cent sulfur dioxide and a corresponding amount of oxygen (1.5 to 3.5 per cent), then thermal decomposition would appear to offer a practical basis for a large scale process. If no decomposition or a slow rate of decomposition occurred, then thermal decomposition would appear very unattractive. In order to follow the progress of decomposition the gypsum was contained in a reactor suspended from a weighing balance.

Reductive decomposition was also studied in the laboratory by passing mixtures of a reducing gas and gaseous products of the decomposition over

heated gypsum. The latter was weighed continuously to follow the progress of the decomposition. When carbon monoxide was the reducing gas, it was assumed that the decomposition proceeded in accordance with the following reaction:

$$CaSO_4 + CO = CaO + SO_2 + CO_2 \qquad (2)$$

Although apparently thermodynamically feasible, experience showed that side reactions leading to the formation of calcium sulfide were a problem. Therefore, the kinetics of reductive decomposition were investigated to see if conditions existed which allowed a reasonably high rate of decomposition while at the same time limiting the sulfide producing reactions.

Raw Materials

The gypsum used in the experimental work was supplied by the United States Gypsum Company from their mine at Fort Dodge, Iowa. The gypsum was crushed and then screened into narrow size fractions. Tyler standard testing sieves were used for the sizing. Each batch was shaken for about 10 minutes by a Ro-Tap Testing Sieve Shaker.

The anhydrite used was some left over from Bollen's work (12) and initially came from an abandoned gypsum mine near Colorado Springs, Colorado. Some of this material was recrushed and screened into the desired size fraction.

The various size fractions of gypsum and anhydrite were analyzed for sulfate and calcium by the same methods used for analyzing the by-product. The following values were found:

Material	Size, mesh	SO_3, %	CaO, %
Gypsum	-3½ +4	45.1	32.0
Gypsum	-6 +8	44.8	31.4
Gypsum	-7 +8	45.0	32.0
Gypsum	-12 +14	45.4	32.1
Anhydrite	-8 +9	53.3	38.2

These values were used as a basis for calculating the conversion or per cent desulfurization.

In order to have a more complete analysis of the gypsum two of the fractions were analyzed by the American Society for Testing Materials standard method, designation C 26-52 (2). The results are presented in Table 4 together with a similar analysis for anhydrite which was obtained by Bollen (12).

Table 4. Analyses of gypsum and anhydrite

	Per cent of sample, dry basis		
Constituent	Gypsum -3½ +4 mesh	Gypsum -7 +8 mesh	Anhydrite[a]
H_2O (combined)	19.4	20.0	5.7
CaO	31.2	31.0	37.1
MgO	0.1	0.1	0
SO_3	45.5	45.3	54.9
CO_2	0.8	0.6	0.4
R_2O_3	0	0	0.2
SiO_2	3.2	3.5	1.6
NaCl	0.3	0.3	0.6
Total	100.5	100.8	100.5

[a]From Bollen (12).

A list of the gases used is given below.

Gas	Manufacturer	Grade	Purity, %
N_2	Air Reduction Co.	water pumped	99.7
N_2 (liquid)	I.S.C. Physics Dept.	-	-
CO	The Matheson Co.	commercial	95.0 min.
CO	The Matheson Co.	c.p.	99.5 min.
H_2	The Balbach Co.	-	99.8
CO_2	Pure Carbonic Co.	-	99.97
SO_2	Ansul Chemical Co.	refrigerant	-
O_2	The Balbach Co.	-	99.5

The purity indicated for these gases is that claimed by the manufacturer. Analysis by means of an Orsat apparatus of the nitrogen supplied by the Air Reduction Company showed that it contained about 0.5 per cent oxygen. On the other hand, similar analyses of the nitrogen obtained as liquid from the Physics Department usually showed this material to contain less than 0.1 per cent oxygen.

For the runs where carbon monoxide was required, the commercial grade was used for the runs numbered 163 and below while the C.P. grade was used for runs numbered 164 and above. Any difference in results due to the grade was not readily apparent.

Apparatus

Equipment was developed for continuously heating and weighing a quantity of gypsum while it decomposed in a stream of gas. Since a

mixture of several gases was usually passed over the gypsum, an extensive train of apparatus was used for drying, filtering, and metering the gases. Moreover, provision was made for heating the gas mixture to the desired reaction temperature before it reached the gypsum.

A flowsheet of the apparatus is shown in Figure 8. Generally, nitrogen gas generated from the liquid state was the major component of the gas mixture. The liquid was stored in either a 10 or 25 liter metal Dewar vacuum flask which was pressurized with nitrogen gas from a high pressure cylinder. The liquid nitrogen was vaporized and the gas dried with anhydrous calcium sulfate and magnesium perchlorate. It was then filtered through glass wool and metered by a rotameter. Drying was probably unnecessary but it was included to guard against the presence of any ice crystals which might have been in the liquid nitrogen. A 5 gallon glass bottle was included in the nitrogen train to provide surge capacity and to stabilize the operation of the nitrogen rotameter.

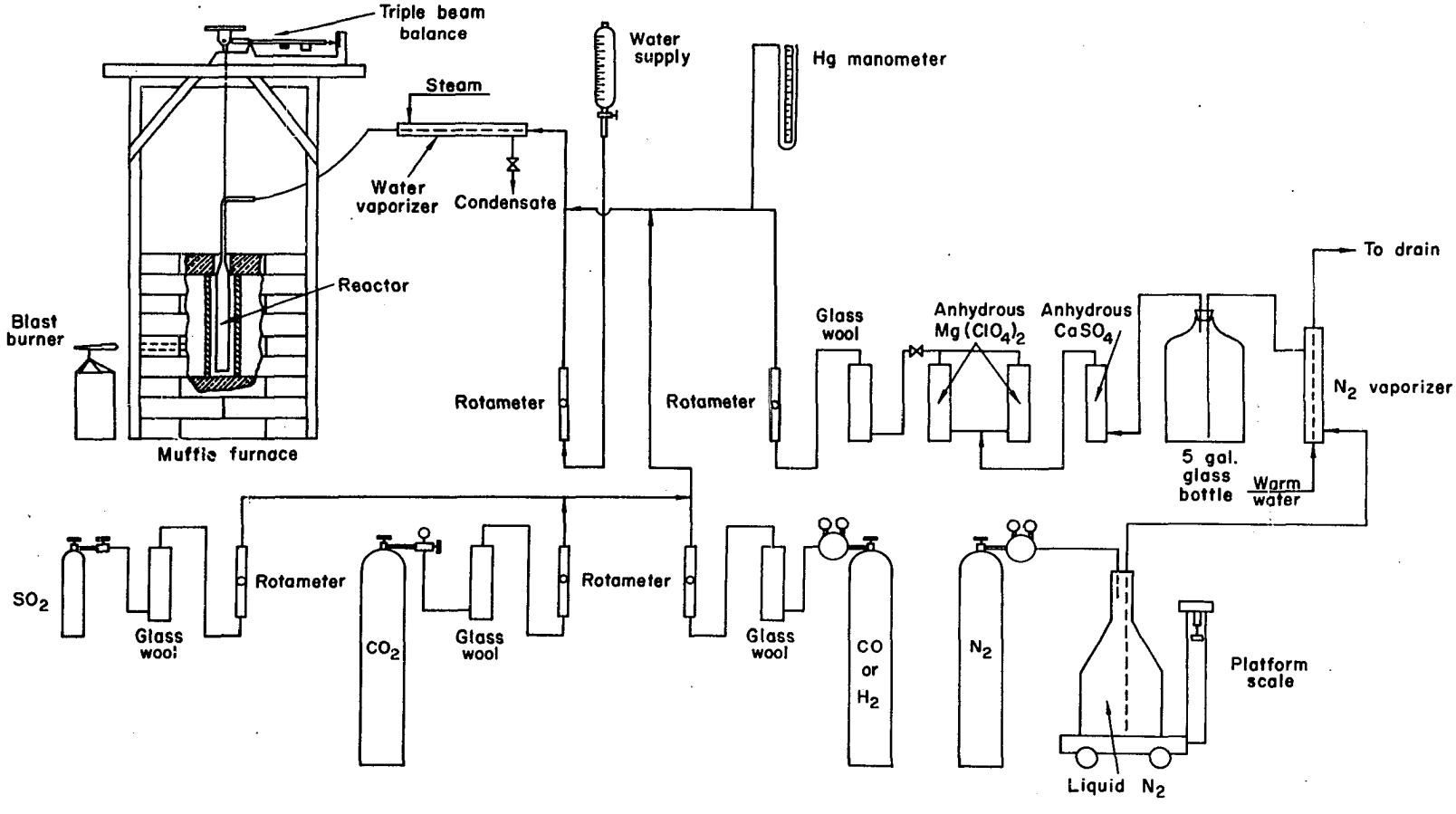
In many of the experiments carbon monoxide, carbon dioxide and sulfur dioxide were components of the gas mixture. These were fed into the system from high pressure cylinders, filtered through glass wool, and metered by rotameters.

For some runs water vapor was a necessary component. When this was the case, distilled water was metered by a rotameter and added to the main gas stream, which was then preheated in a double pipe heat exchanger to insure complete vaporization of the water before it reached the reactor.

When hydrogen was used, a hydrogen cylinder was substituted for the carbon monoxide cylinder.

If the occasion demanded it, oxygen was also added. It was supplied

Figure 8. Flowsheet of the apparatus used for the laboratory investigation


Triple beam balance
Steam
Water supply
Hg manometer
Water vaporizer
Condensate
Reactor
Blast burner
Muffle furnace
Rotameter
Rotameter
Glass wool
Anhydrous $Mg(ClO_4)_2$
Anhydrous $CaSO_4$
To drain
N_2 vaporizer
5 gal. glass bottle
Warm water
SO_2
Glass wool
Rotameter
CO_2
Glass wool
Rotameter
Glass wool
CO or H_2
N_2
Platform scale
Liquid N_2

from a high pressure cylinder, filtered and metered in the same manner as the other compressed gases.

Reactors

A vertical tube reactor was built from refractory materials having both high temperature and thermal shock resistance. It is shown in Figure 9. The tube forming the outer shell was a zirconium silicate combustion tube made by the Laboratory Equipment Corporation. This was cut to the proper length and drilled for a 0.156 inch diameter ceramic thermocouple insulator. In the center of this insulator was located a butt-welded chromel-alumel thermocouple junction made of either 20 or 22 A.W.G. gauge thermocouple wires. A glass elbow was attached to the small end of the zircon tube with silicone rubber tubing or with glass cloth tape. The large end of the zircon tube was closed by a packing support grid made out of silica rods. The grid was held in place with chromel wires and in operation it supported the contents of the reactor.

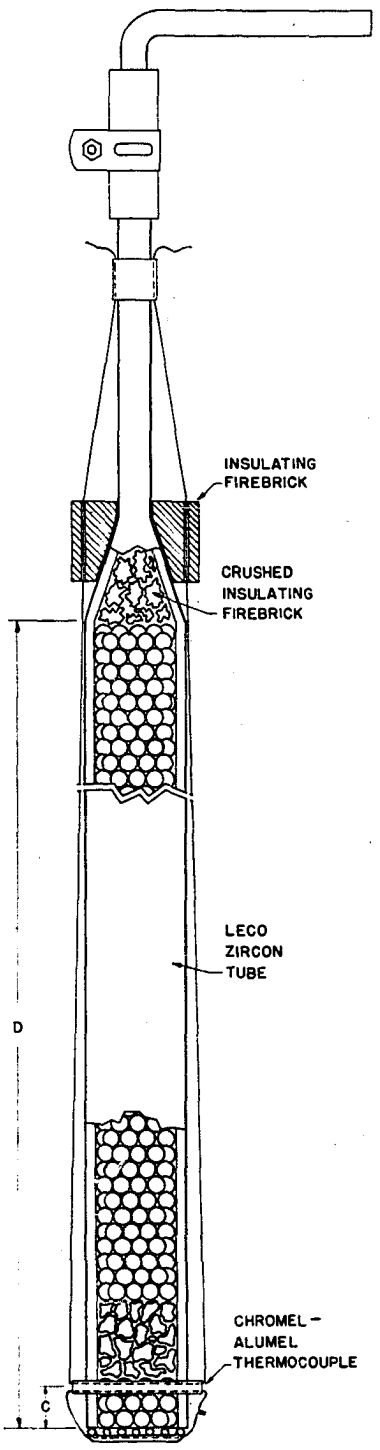
Several layers of tabular alumina balls (-3 +4 mesh) were placed on top of the packing support and the gypsum particles were placed on top of the alumina balls. The remainder of the reactor was filled with additional alumina balls, which served as a heat transfer medium. A few pieces of crushed insulating firebrick were placed above the balls for support of the reactor contents when it was inverted for filling or emptying.

During operation the reactor was hung vertically from a triple beam balance located directly above the reactor. The main body of the reactor was surrounded by a furnace. A piece of insulating firebrick served to partly close the furnace opening and shield the reactor gas connection

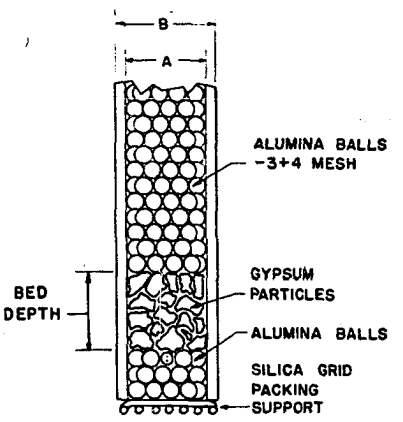
Figure 9. Ceramic vertical tube reactor

REACTOR DIMENSIONS, INCHES

REACTOR	A	B	C	D
A	1.03	1.29	0.49	12
B	1.15	1.39	0.56	10
C	1.03	1.28	0.50	11
E	0.98	1.20	0.72	11
F	1.09	1.38	0.69	11
G	0.93	1.20	0.63	11
H	0.98	1.20	0.47	11
I	1.10	1.36	0.63	11
J	1.14	1.39	1.61	12
K	1.15	1.37	1.63	12
L	1.10	1.36	0.44	10-1/8
M	0.99	1.20	1.63	12
N	0.75	1.03	1.63	16-1/4
O	0.75	1.03	1.59	16-1/2
P	0.97	1.20	1.64	12
Q	1.13	1.36	1.61	12



FRONT



SIDE

from furnace radiation.

Sixteen reactors were built and used. They differed somewhat in size and a list of their dimensions accompanies Figure 9. Reactor H was unusual in that it was equipped with two thermocouples. The second thermocouple was located 1.03 inch above the first, which was in the usual position.

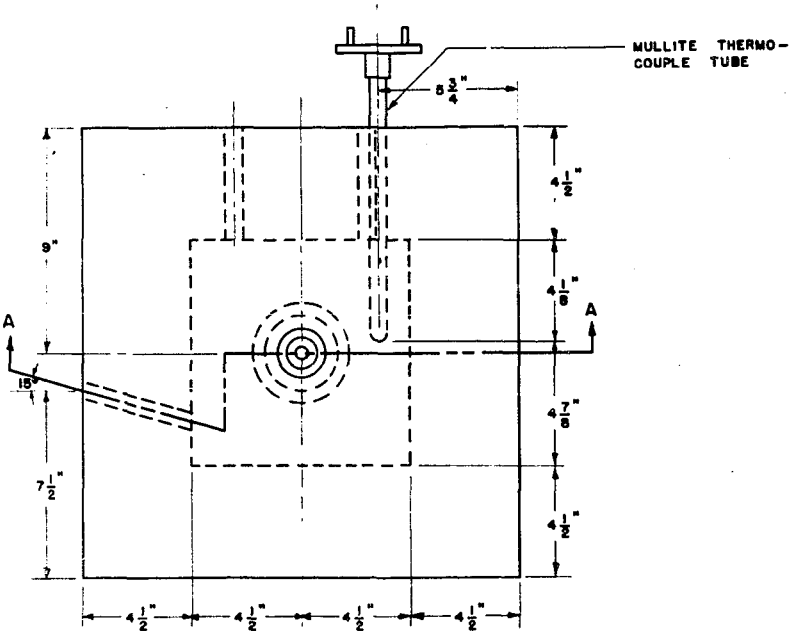
Furnace

For heating the reactor the gas fired muffle furnace shown in Figure 10 was built of K-28 insulating firebrick. A cylindrical refractory tube of fused magnesia was used for a muffle. This tube isolated the reactor from the combustion space and provided a surrounding of relatively uniform temperature for the reactor. A laboratory blast burner was used to introduce a mixture of natural gas and air through a hole in the side of the furnace. At operating temperature surface combustion occurred on the surfaces enclosing the combustion chamber. Two holes were placed in the back of the furnace for escape of the exhaust gases. The reactor was placed inside the muffle through an opening in the top of the furnace.

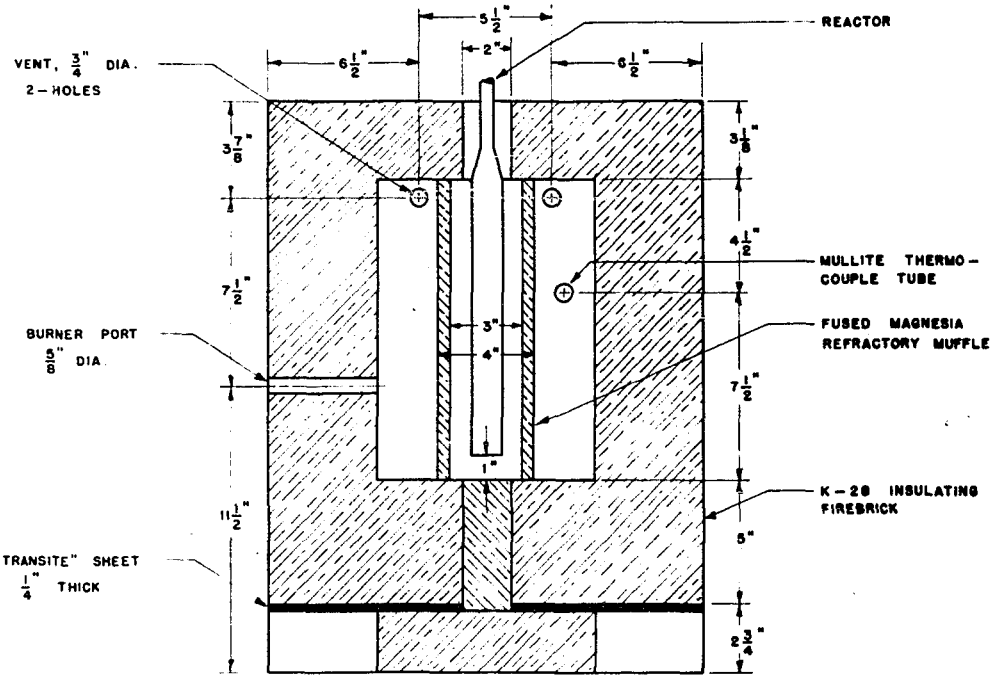
A platinum-platinum, 13 per cent rhodium thermocouple in a mullite protection tube was positioned in the combustion space and connected to a Brown temperature recorder. This was used as an aid in controlling the furnace temperature.

Figure 11 is a photograph of the furnace, reactor, balance, and framework.

Figure 10. Details of gas fired muffle furnace



PLAN VIEW



SECTION A-A

Figure 11. Muffle furnace and arrangement for weighing reactor

Experimental Procedure

Thermal decomposition

Inert or neutral atmosphere A reactor was charged with gypsum particles of the proper size to provide the desired bed depth. The weight of gypsum in the charge was noted. After the furnace reached operating temperature, the reactor was suspended inside the furnace from the triple beam balance and a small stream of air was passed through the reactor while it was heating. Shortly before the reactor reached the desired operating temperature the air stream was stopped and nitrogen was introduced. The time, reactor weight and temperature were immediately noted. The furnace was controlled so that the reactor temperature could be made to approach the desired temperature without overshooting. At regular intervals of 5 or 10 minutes the time, reactor weight and temperature, and other important conditions were recorded. Operating conditions were kept as constant as possible while a run was in progress. The runs were usually continued until the reactor reached a constant weight, but in a few instances they were stopped short of this. If the run was stopped before a constant weight was reached, air was substituted for nitrogen while the reactor was withdrawn from the furnace. About 15 minutes were taken to withdraw the reactor in order to reduce the thermal shock. After the reactor was raised feeding of gas was stopped and the reactor was placed aside to cool. The charge was subsequently recovered and analyzed for sulfate and calcium.

In a couple of runs carbon dioxide was substituted for nitrogen, but otherwise the procedure was the same.

Decomposition products atmosphere In order to test the equilibrium several runs were made in which gaseous mixtures of sulfur dioxide, oxygen, and nitrogen were fed. The prerun and postrun parts of the procedure were the same as described above. However, at the beginning of the run sulfur dioxide, oxygen and nitrogen were introduced. Instead of maintaining constant conditions throughout the run, either the temperature or gas composition was varied and sometimes both.

Reductive decomposition

A reactor was charged with sufficient particulate gypsum of the proper size to provide the desired bed depth, usually 1 inch. The weight of gypsum in the charge was noted. After the furnace reached operating temperature, the reactor was suspended inside the furnace from the triple beam balance. During the initial stage of heating air was passed through the reactor; during the final stage a mixture of air and sulfur dioxide was used. These gases prevented the gypsum from decomposing before the run started. Shortly before operating temperature was reached, nitrogen and carbon dioxide were added to the mixture. After the reactor temperature had leveled out at the desired point, the air flow was stopped and the sulfur dioxide feed rate was readjusted. Carbon monoxide was then introduced. This marked the beginning of the run. At regular intervals of 1 to 10 minutes, depending on the rate of reaction, the time, reactor weight and temperature, and other important conditions were recorded. During the run every effort was made to maintain constant conditions. The run ended when the reactor reached a constant weight. While the reactor was being withdrawn from the furnace, only nitrogen and a very

small amount of carbon monoxide were fed. To prevent the reactor from cracking due to thermal shock, it was raised slowly over about a 15 minute period. After the reactor was completely raised, the gas flow was stopped and the reactor was placed aside to cool. The charge was subsequently recovered and analyzed for sulfate, sulfide, and calcium.

The procedure was the same when hydrogen was used in place of carbon monoxide or when water vapor was used in place of carbon dioxide.

Methods of Analysis

Sulfate in the product was determined gravimetrically by precipitation as barium sulfate in accordance with the method outlined by the American Society for Testing Materials (2).

Sulfur present in the form of calcium sulfide was determined by an iodometric method. The sample was placed in a flask and an excess of a standard solution of the two salts potassium iodate and potassium iodide was added. An excess of hydrochloric acid was subsequently added and the flask tightly stoppered. The effect of the acid was to liberate hydrogen sulfide from the sample and free iodine from the iodide-iodate mixture. The hydrogen sulfide and free iodine in turn reacted with each other. The final step in the determination was the titration of the excess iodine with standard sodium thiosulfate solution.

Calcium was determined by the versenate titration method developed for determining total hardness in water, described by Diehl, Goetz and Hach (23). The adaptation of the method to the determination of calcium in gypsum is discussed by Bollen (12).

Results

In carrying out a run it was possible to control the charge weight, particle size, bed dimensions, gas mass velocity or feed rate, gas composition, and bed outlet temperature. During a run the weight lost by the charge was measured as a function of the elapsed time. After analyzing the solid product from a run it was possible to calculate the total conversion of calcium sulfate to calcium oxide. This was called the total desulfurization. At any given instant during a run the desulfurization was proportional to the weight lost by the charge. This was not necessarily true for the case where part of the charge was converted to calcium sulfide. Nevertheless the assumption of proportionality was always made so that at least some estimate of the functional relationship between conversion and time was obtained. The slope of the curve expressing this relationship was the rate of conversion or the desulfurization rate.

The desulfurization rate varied as a given batch of gypsum was converted. However, in practically every case during an appreciable part of the run the batch decomposed at a constant rate which was also the maximum rate for the run. Sometimes the maximum rate period would be observed at the beginning and sometimes in the middle of the run. If the latter occurred, it was quite common for a second constant but slower rate period to appear at the beginning of the run.

In general it was found that the desulfurization rates corresponding with the constant rate periods could be correlated with experimental conditions. Similarly the percentage of calcium sulfide in the product could

also be correlated. These results are summarized in Table 18 in the Appendix, together with experimental conditions for all the runs. The headings of this table are self-explanatory with the possible exception of the one entitled "gas composition", which refers to the composition of the gas fed to the reactor. When the initial and maximum desulfurization rates were one and the same, the same value is listed under both headings. The temperatures listed are average bed exit temperatures corresponding to the constant rate periods.

Thermal decomposition

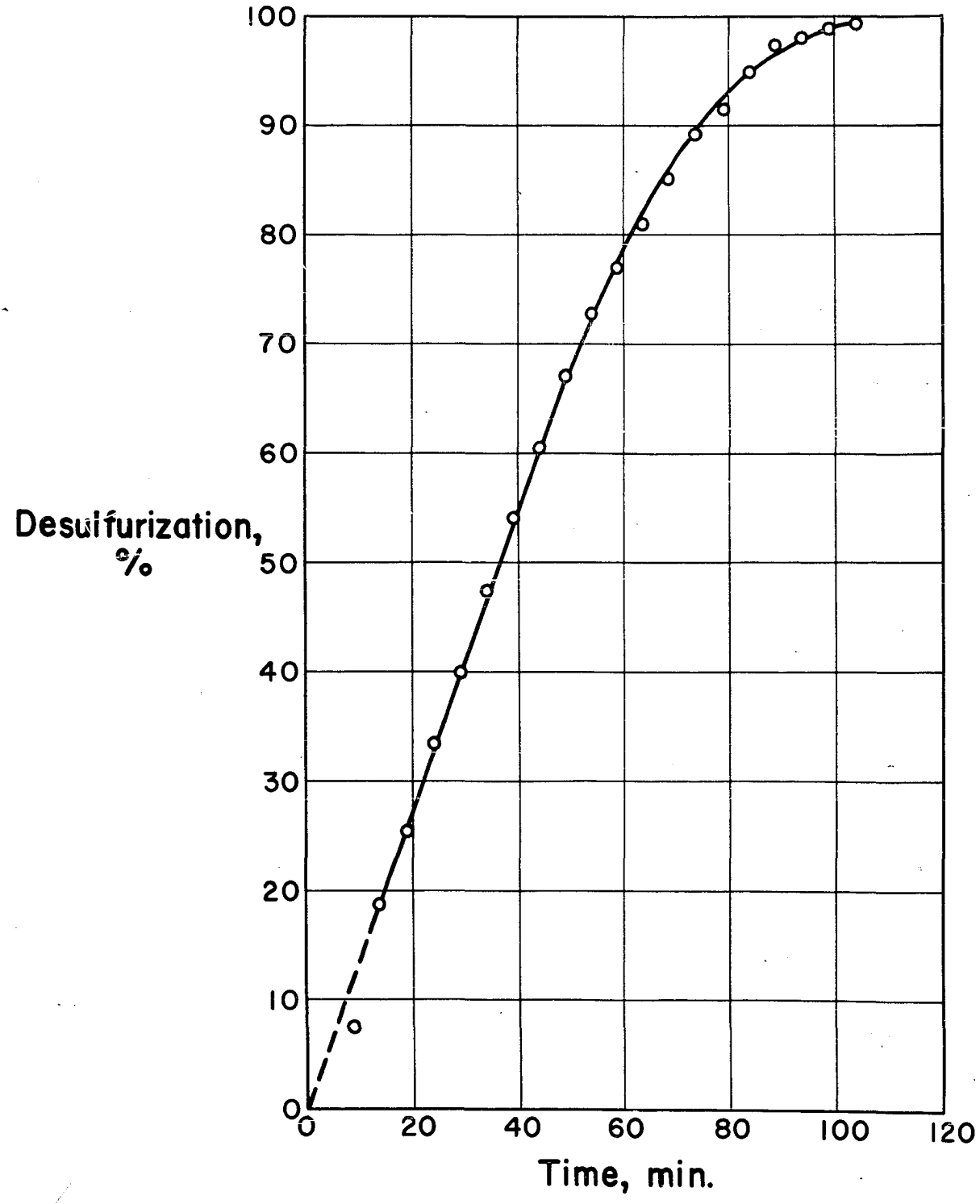
Desulfurization rate Several runs were made in which relatively pure nitrogen or carbon dioxide was passed over gypsum heated to temperatures between 2100 and 2300°F. In a typical run the gypsum decomposed at a constant rate until it was about half desulfurized, whereupon the rate gradually diminished to zero as complete desulfurization was approached. The relationship between the desulfurization and the elapsed time for such a run is presented in Figure 12. This type of relationship will be referred to as a desulfurization curve. Its slope is the rate of desulfurization.

When an inert atmosphere was employed, the initial constant rate period coincided with the period during which the gypsum decomposed at the maximum rate. The latter appeared to vary according to the experimental conditions. For example, the maximum rate seemed to increase with temperature and gas velocity, but the presence of as little as 0.5 per cent oxygen impurity in the nitrogen appeared to reduce the rate.

At the upper limits of temperature, gas velocity, and nitrogen purity

Figure 12. Desulfurization curve for gypsum in an inert atmosphere

gas composition, 100% N_2
temperature, 2240°F
mass velocity, 0.11 lb./sec. x sq.ft.
gypsum size, -6 +8 mesh
bed depth, 1.63 in.


Desulfurization, %
100
90
80
70
60
50
40
30
20
10
0
0
20
40
60
80
100
120
Time, min.

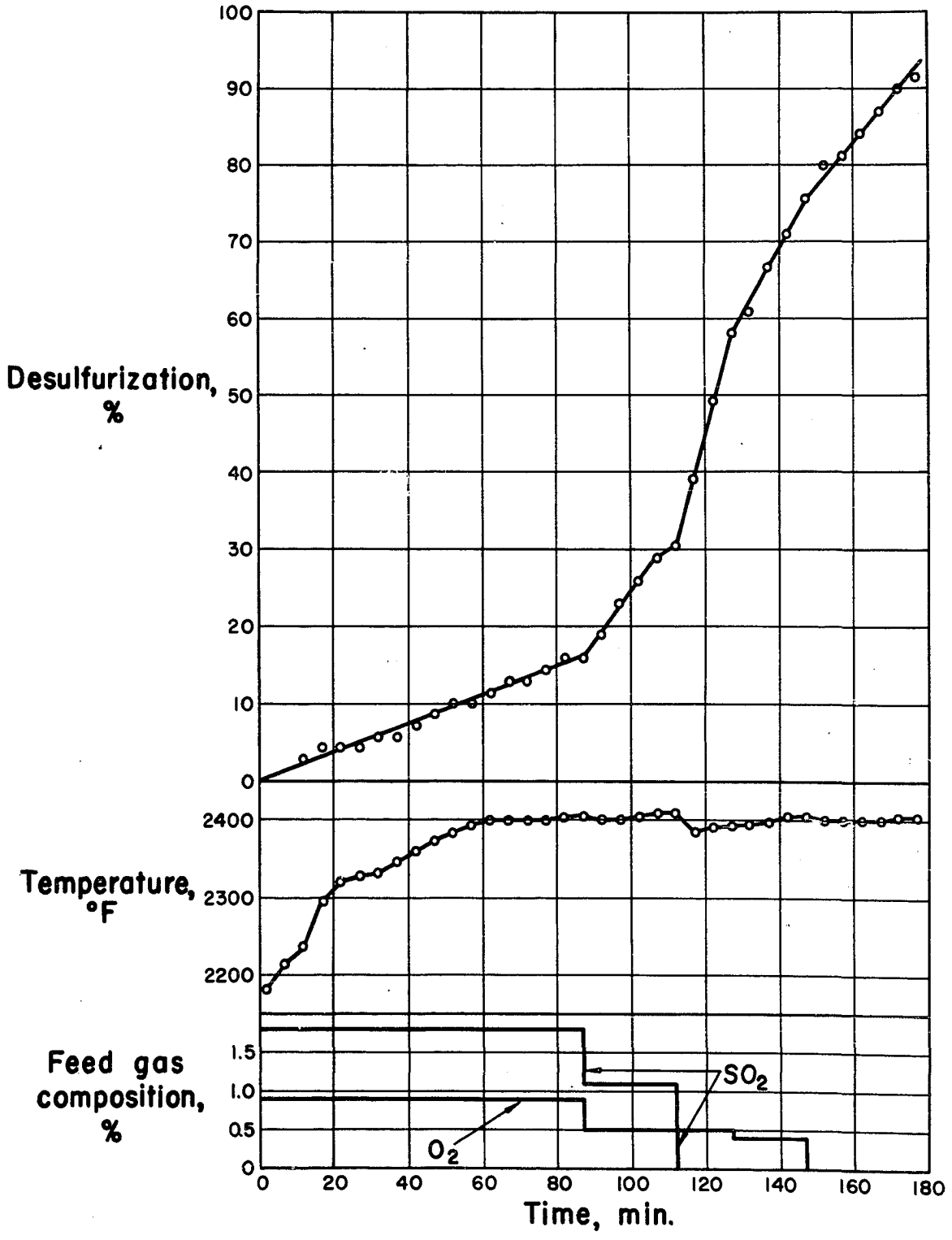
virtually complete desulfurization of the gypsum was obtained in 1 hour or less. It was apparent then that the rate of decomposition would not limit a process based on thermal decomposition. However, these experiments did not demonstrate whether or not the equilibrium was favorable. For this purpose it was necessary to carry out some additional experiments which are discussed below.

Test of equilibrium In order to test the decomposition equilibrium of gypsum, several samples were heated to temperatures in the range of 2100 to 2400°F while exposed to an atmosphere of products of the decomposition, sulfur dioxide and oxygen. Various concentrations of these gases, diluted with nitrogen, were passed through the gypsum. A loss in weight meant that the sum of the partial pressures of sulfur dioxide and oxygen in the feed gas was not as large as the decomposition pressure of the gypsum.

The results of the first experiment are presented in Figure 13. The bed outlet temperature, composition of the gas fed, and the resulting desulfurization are plotted against time. During the first 87 minutes the gypsum decomposed slowly at a constant rate while a gas mixture containing 1.8 per cent sulfur dioxide and 0.9 per cent oxygen was passed over it. Since the temperature increased from 2160 to 2400°F during this interval, it seemed anomalous for the desulfurization rate to remain constant. An increase in the rate of decomposition was obtained by reducing the concentrations of both sulfur dioxide and oxygen. A second constant rate period followed. A still higher rate was observed when sulfur dioxide was eliminated from the feed. When oxygen was eliminated near the end of the run, little effect on the rate was observed.

Figure 13. Desulfurization of gypsum, Run 27

mass velocity, 0.12 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Desulfurization, %
100
90
80
70
60
50
40
30
20
10
0
Temperature, °F
2400
2300
2200
Feed gas composition, %
1.5
1.0
0.5
0
SO_2
O_2
0
20
40
60
80
100
120
140
160
180
Time, min.

In the second experiment the sample was heated rapidly to 2300°F with essentially no decomposition occurring. While the gypsum was held at a constant temperature, a gas mixture containing 0.5 per cent sulfur dioxide and 0.25 per cent oxygen was passed over it. The results are shown in Figure 14. Some desulfurization was observed at first but after 22 minutes decomposition stopped. Eliminating oxygen from the feed failed to produce a reaction. However, a subsequent reduction in the sulfur dioxide concentration did coincide with a resumption in desulfurization.

A third experiment was performed in which a gas mixture containing 0.26 per cent sulfur dioxide and 0.14 per cent oxygen was passed over gypsum while it was slowly heated from 2050 to 2220°F. The results are shown in Figure 15 and indicate only a slight decomposition of the sample during the 95 minute period.

These experiments demonstrated that even small concentrations of the decomposition products either prevented the thermal decomposition of gypsum or at least reduced the rate of decomposition to an impracticably low level. Since gypsum decomposed at an appreciable rate in a neutral atmosphere, it seemed probable that it did not decompose in an atmosphere of decomposition products because of an unfavorable equilibrium.

Reductive decomposition

Although there are several reducing gases which might be appropriate for use in reductive decomposition, only carbon monoxide was investigated extensively. A few runs were made with hydrogen but this resulted in such high reaction rates that control and measurement of bed temperature and measurement of the decomposition rate were impractical except for very

Figure 14. Desulfurization of gypsum, Run 28

temperature, 2300°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

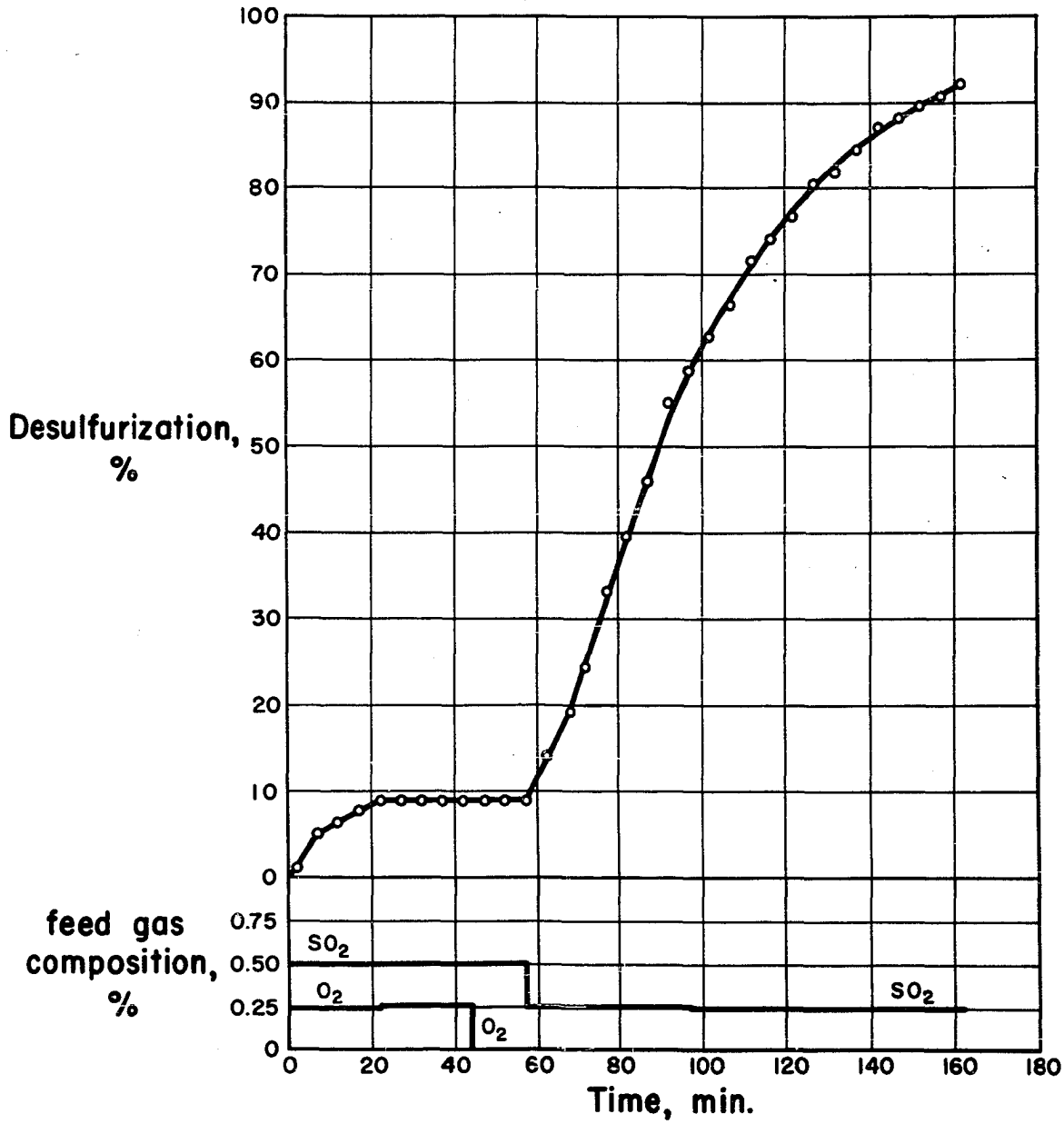
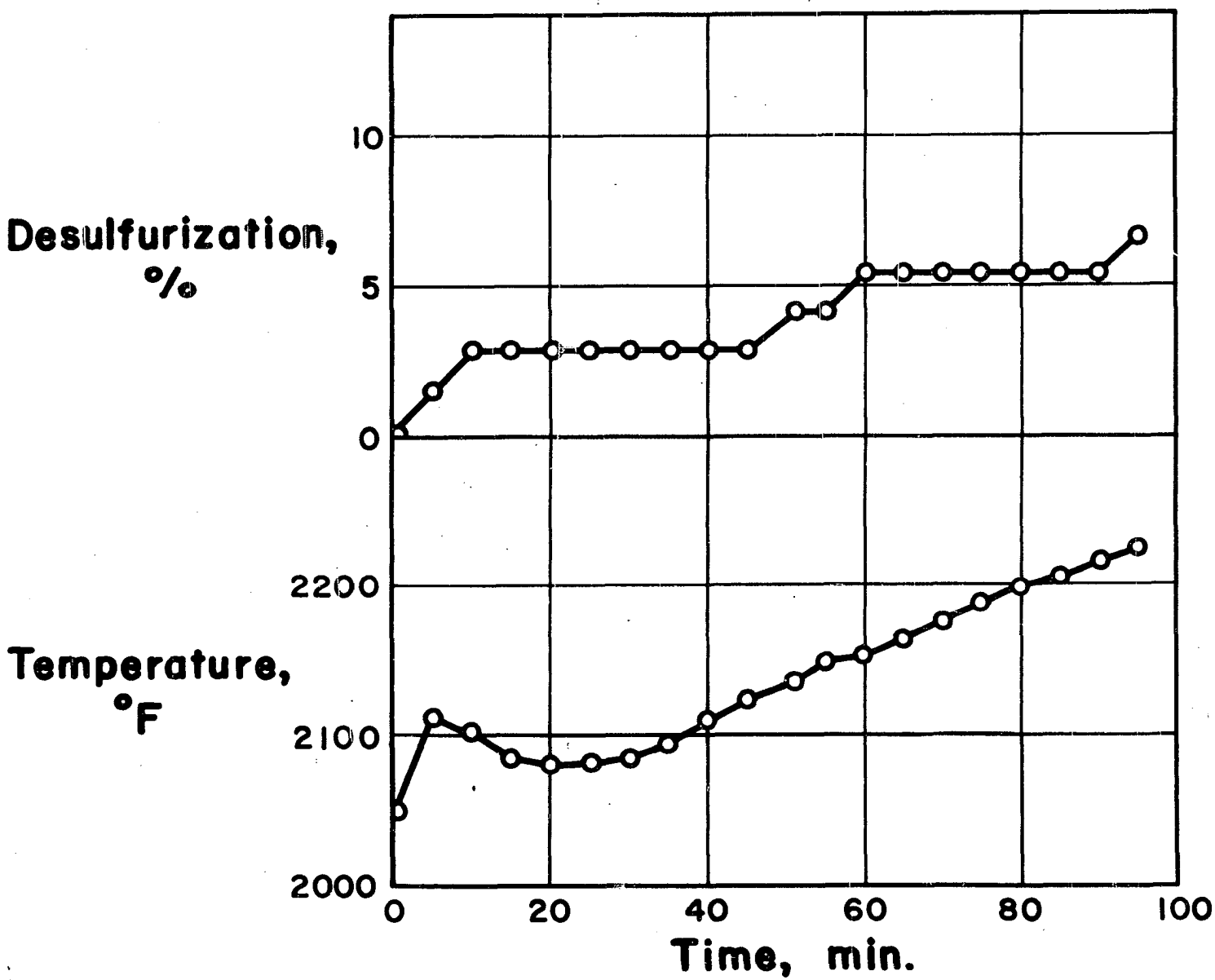

Desulfurization, %
100
90
80
70
60
50
40
30
20
10
0
feed gas composition, %
0.75
0.50
0.25
0
SO2
O2
O2
SO2
0
20
40
60
80
100
120
140
160
180
Time, min.

Figure 15. Desulfurization of gypsum, Run 29

gas composition, 0.14% O_2, 0.26% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Desulfurization, %
Temperature, °F
10
5
0
2200
2100
2000
0
20
40
60
80
100
Time, min.

low concentrations (1 or 2 per cent) of hydrogen.

The effect of temperature, mass velocity, particle size, and gas composition on the desulfurization rate was explored for a limited range of conditions. In addition, the effect of temperature and gas composition on the percentage of residual calcium sulfide in the solids was investigated. Some work was also carried out to determine possible differences in the behavior of anhydrite and gypsum, water vapor and carbon dioxide, and hydrogen and carbon monoxide.

Character of desulfurization curves In general two distinct types of desulfurization curves were obtained. When the gas fed to the reactor was a mixture of carbon monoxide and nitrogen either with or without carbon dioxide, the type of curve shown in Figure 16 was usually observed. In other words the gypsum decomposed from the start at a constant rate which was also the maximum rate. The curve was similar to those observed when only nitrogen was passed over heated gypsum.

A different type of curve resulted when sulfur dioxide was included in the feed gas. The second type is shown in Figure 17. The curve resembled an elongated "S" or integral sign. In some cases the transition from the initial constant rate period to the maximum constant rate period was quite sharp while in others it was a gradual change. As the carbon monoxide concentration increased the length of the initial constant rate period decreased. With 5 per cent sulfur dioxide and more than 5 per cent carbon monoxide in the feed gas the desulfurization curves resembled the first type.

Apparently the presence of sulfur dioxide in the feed gas is not necessary to produce curves of the second type. When a gas mixture con-

Figure 16. Desulfurization curve for gypsum in a reducing atmosphere

gas composition, 4% CO, 15% CO_2, 0% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

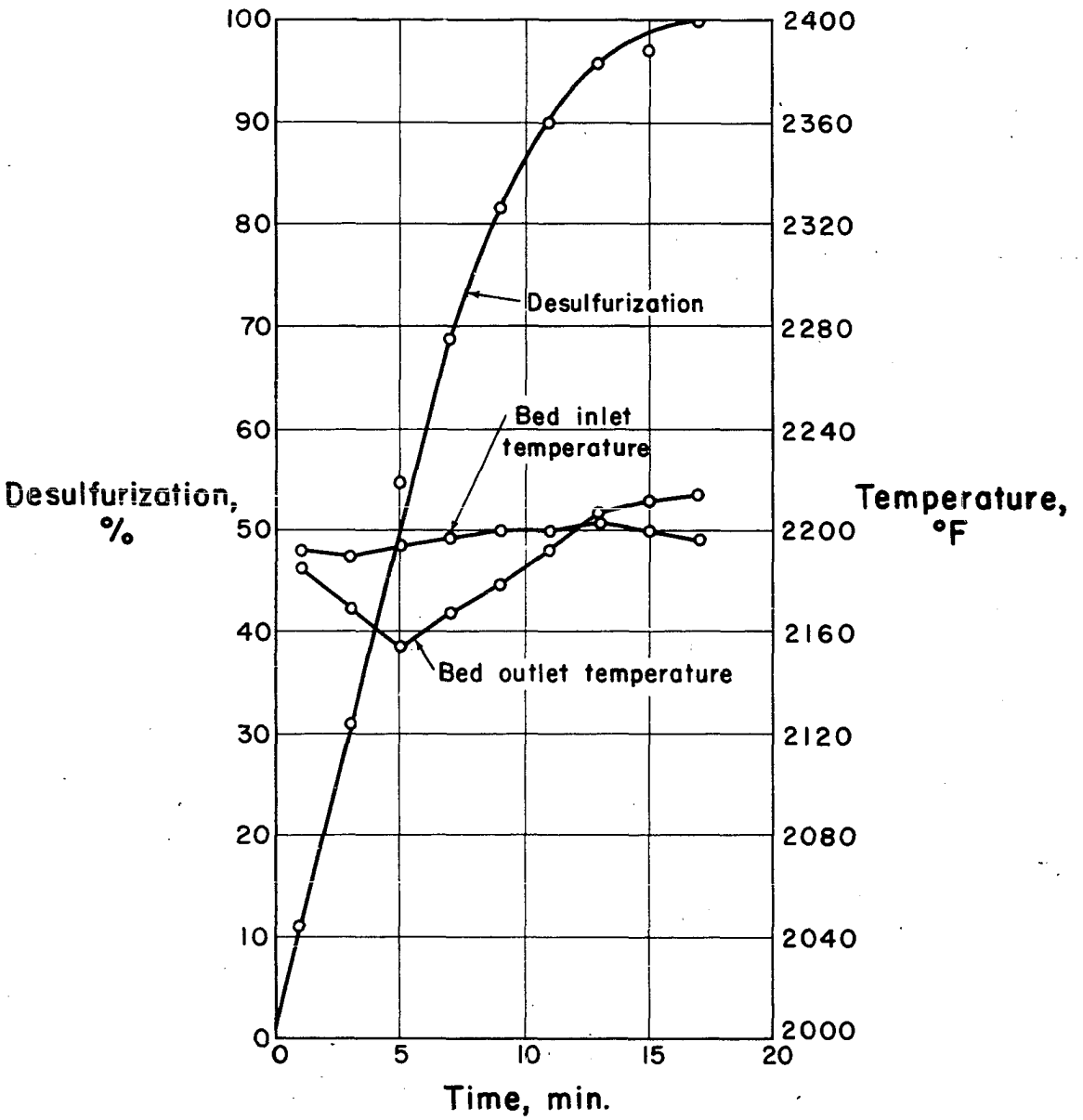
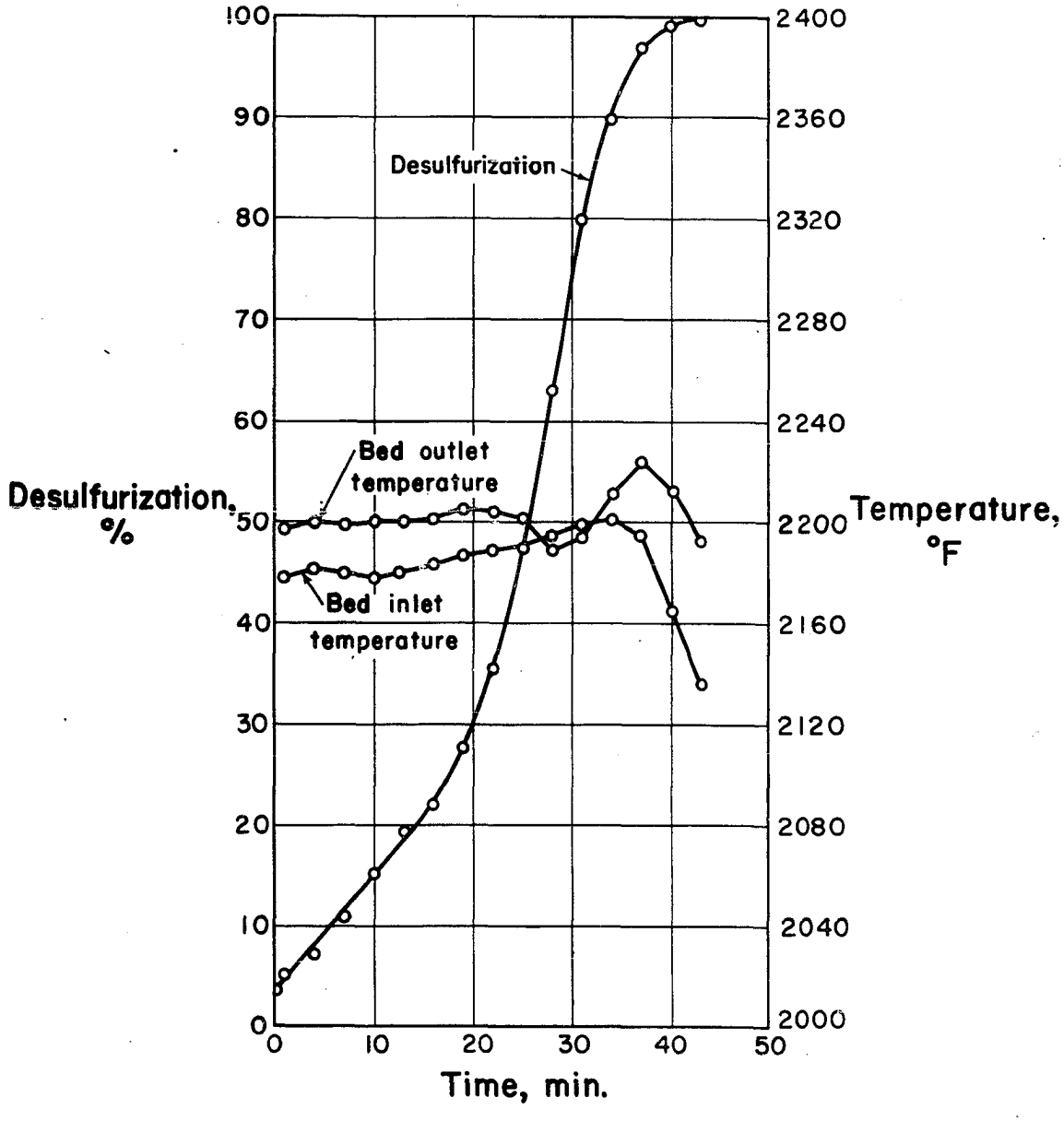

Desulfurization, %
Temperature, °F
Time, min.
Desulfurization
Bed inlet temperature
Bed outlet temperature
100
90
80
70
60
50
40
30
20
10
0
2400
2360
2320
2280
2240
2200
2160
2120
2080
2040
2000
0
5
10
15
20

Figure 17. Desulfurization curve for gypsum in a reducing atmosphere containing sulfur dioxide

gas composition, 3% CO, 20% CO_2, 5% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Desulfurization, %
Temperature, °F
Time, min.
Desulfurization
Bed outlet temperature
Bed inlet temperature
100
90
80
70
60
50
40
30
20
10
0
2400
2360
2320
2280
2240
2200
2160
2120
2080
2040
2000
0
10
20
30
40
50

taining 2 per cent carbon monoxide and 5 per cent carbon dioxide was passed over gypsum heated to 2100°F, the lower end of the temperature range explored, curves of the second type were obtained. At 2200°F and other conditions the same, the curves were of the first type.

Temperature variation The temperature of the muffle furnace could be controlled fairly well and the temperature of the gas entering the bed of gypsum could also be closely controlled. However, due to the endothermic nature of the decomposition reaction there was considerable variation in the temperature drop across the gypsum bed. The temperature drop varied with the decomposition rate.

Before the start of a typical run the temperature on the gas outlet side of the gypsum bed would be higher than on the gas inlet side. After decomposition set in, the outlet temperature would start falling, and if the desulfurization rate was relatively rapid, the outlet temperature might fall considerably below the inlet temperature. The bed outlet temperature would reach a minimum when the gypsum was about half desulfurized and then it would start increasing. By the end of the run it would exceed the inlet temperature again. This pattern is shown in both Figures 16 and 17. As previously mentioned, the drop in the outlet temperature was a function of the decomposition rate so that for a rate of 15 per cent per minute, which was relatively fast, the temperature drop across the bed reached a maximum value of 90°F.

All but one of the reactors had a single thermocouple which was located on the gas outlet side of the gypsum bed. It was necessary, therefore, to use the bed outlet temperature for correlating the results.

Bed dimensions Most of the runs were made with a gypsum bed

depth of 1.0 inch. A few were made with a bed depth of 0.5 inch. Although the difference in bed depth may have affected the results in some cases, the effect seemed to be small in comparison with the experimental error.

During the investigation reactors having different diameters were used indiscriminately. In most cases there was no noticeable effect in the results due to differences in the diameter. However, some effect was observed for the case of runs made with a feed gas containing 2 per cent carbon monoxide and various amounts of carbon dioxide and sulfur dioxide. The results of this particular set of runs are presented in Table 5. A comparison of the results shows that an increase in the reactor diameter had the effect of decreasing the desulfurization rate which in turn resulted in a conspicuous increase in the time required for run completion. In two out of three pairs of values listed, an increase in diameter seemed to cause an increase in the per cent of calcium sulfide found in the solids.

It is not easy to explain why the diameter should affect the results. Perhaps peripheral channeling of the gas flow was the cause. This might have resulted in a larger core of slowly moving gas in the center of the larger diameter reactor than in the smaller reactor.

Since the experimental accuracy seemed to vary inversely with the decomposition rate, the relatively small effect of reactor diameter was apparently revealed by a set of runs which had some of the slowest decomposition rates observed.

Correlation of desulfurization rates Since all of the desulfurization curves exhibited one or two straight line portions, it proved convenient to correlate the corresponding desulfurization rates with

Table 5. Effect of reactor diameter

(-7 +8 mesh gypsum, 1 in. bed depth, 2200°F, mass vel. = 0.20 lb./sec. x ft.^{2})

Run no.	Dia. in.	Charge grams	Gas composition[a] mole % CO	CO_2	SO_2	CaS %	Desulfurization rate, %/min. Initial	Max.	Total[b] min.
169	1.14	20.1	2.0	10.0	1.0	0.59	0.62	1.43	107
187	0.75	9.6	2.0	9.9	1.0	0.66	0.83	1.93	66
115	1.15	22.7	2.0	10.0	2.0	0.74	0.24	1.69	131
186	0.75	9.4	2.0	9.8	2.0	0.33	0.32	1.87	93
168	0.97	15.3	2.0	19.8	5.0	1.79	0.13	1.18	185
163	0.75	9.0	2.1	19.7	5.0	1.10	0.30	1.38	106

[a]Remainder nitrogen.

[b]Total time required to complete run.

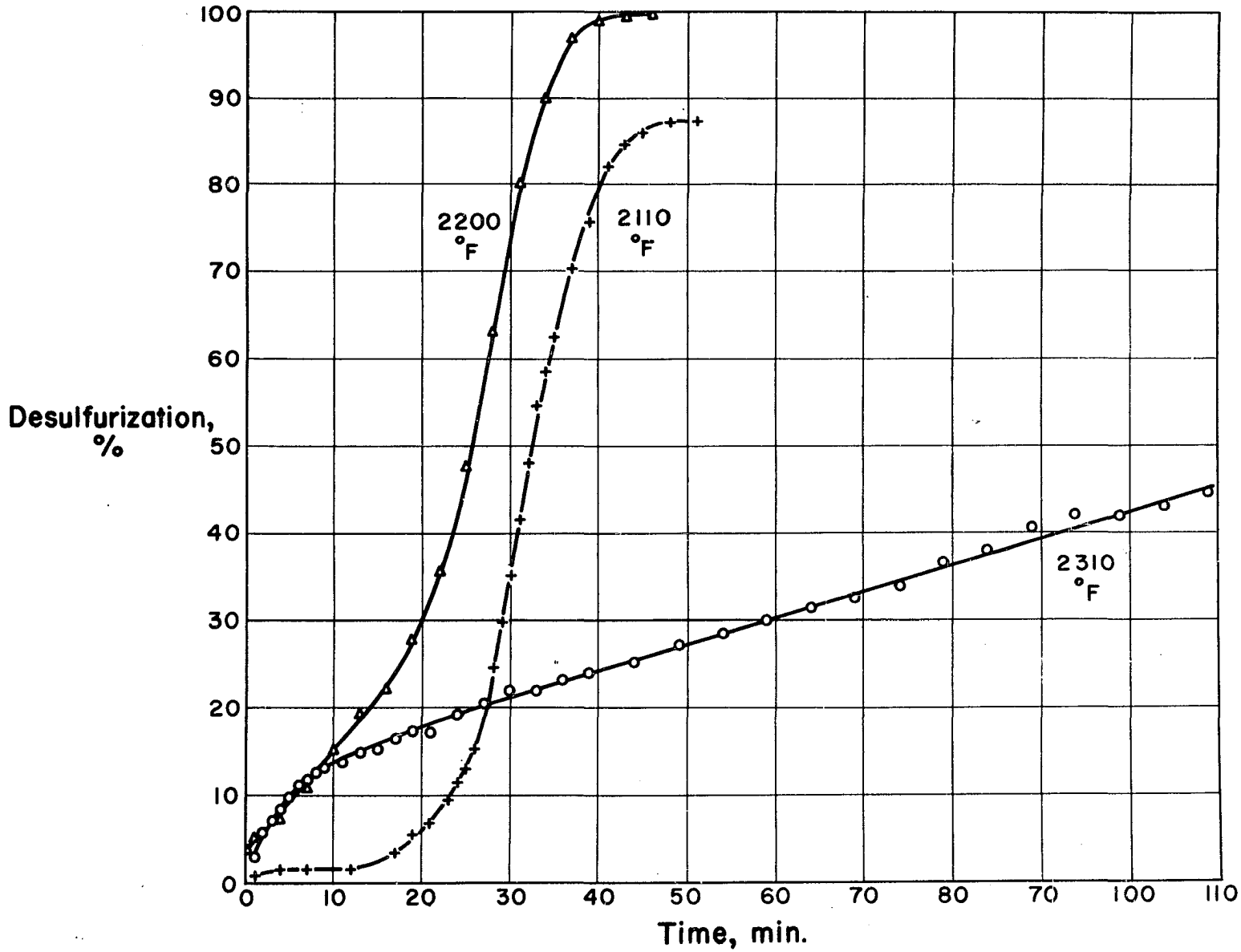
experimental conditions. It was possible thereby to show how the initial and maximum rates were affected by different levels of temperature, etc. Not determined was the mechanism responsible for the change in decomposition rate which produced the unusual "S" shape of many desulfurization curves.

Effect of temperature The effect of temperature on desulfurization rate was explored in the range of 2100 to 2300°F for single values of mass velocity and particle size and for various gas compositions.

The desulfurization curves obtained at different temperatures when the gas fed contained 3 per cent carbon monoxide, 20 per cent carbon dioxide, and 5 per cent sulfur dioxide are plotted in Figure 18. At 2110

Figure 18. Effect of temperature on the desulfurization curves

gas composition, 3% CO, 20% CO_2, 5% SO_2
temperature, 2110°F (Run 202), 2200°F (Run 117), 2310°F (Run 198)
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

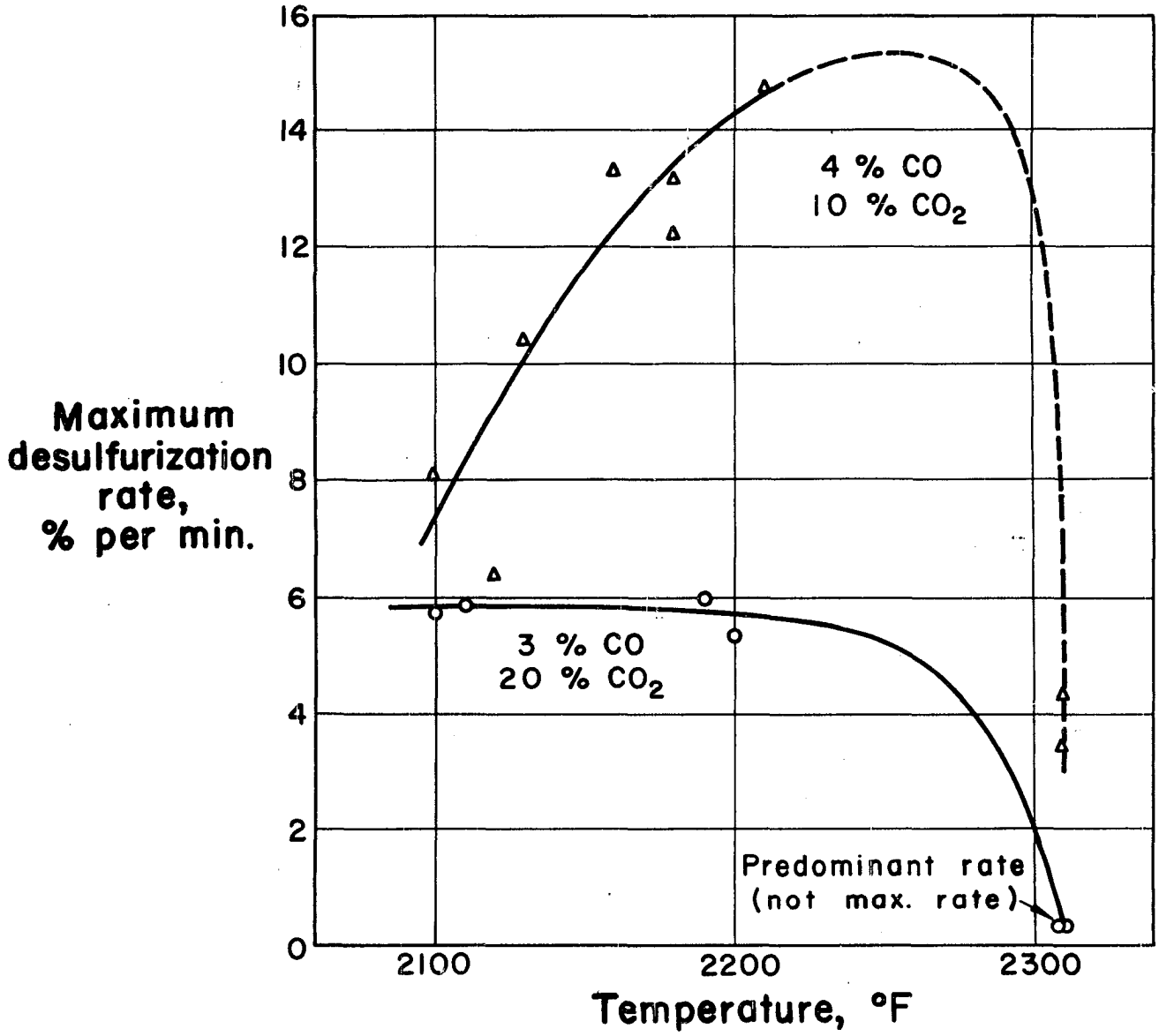

Desulfurization, %
100
90
80
70
60
50
40
30
20
10
0
0
10
20
30
40
50
60
70
80
70
100
110
Time, min.
2200 °F
2110 °F
2310 °F

and 2200°F the curves were "S" shaped but at 2310°F an entirely different type of curve was obtained. Thus for the highest temperature the desulfurization rate was rapid at the start but it soon fell to a much lower but constant value which was maintained until the run was stopped. Although this type of curve could be reproduced for the same conditions, it was not observed for any other conditions covered by the investigation. A comparison of the curves for the two lower temperatures shows that although their central portions were nearly parallel, the slopes of their initial portions differed greatly. In other words, the difference in temperature had a much greater effect on the initial desulfurization rate than on the maximum rate. At the lowest temperature the gypsum seemed to pass through an induction period of several minutes before it started to decompose. On the basis of conversion, the maximum rate predominated at the lower temperature levels while the minimum rate seemed to predominate at the highest temperature. When the dominant rates were plotted against temperature, the lower curve in Figure 19 was obtained. Thus for the particular gas composition it appears that the predominant rate is independent of temperature between 2100 and 2200°F but falls rapidly at higher temperatures to nearly zero value.

A slight change in the gas composition resulted in an entirely different relationship between the desulfurization rate and temperature. When the reactor feed gas contained 4 per cent carbon monoxide, 10 per cent carbon dioxide, and 5 per cent sulfur dioxide, the upper curve in Figure 19 was obtained. In this instance the maximum rate almost doubled as the temperature was increased from 2100 to 2200°F. At some temperature between 2200 and 2300°F the rate reached a maximum value and then dropped.

Figure 19. Effect of temperature on the maximum desulfurization rate

gas composition, 5% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh


Maximum desulfurization rate, % per min.
16
14
12
10
8
6
4
2
0
4 % CO
10 % CO2
3 % CO
20 % CO2
Predominant rate
(not max. rate)
2100
2200
2300
Temperature, °F

At 2310°F the rate was lower than at 2100°F. For this gas composition the desulfurization curves had the same general "S" shape throughout the range of temperature explored. The effect of temperature on the initial desulfurization rate is illustrated in Figure 20. It is interesting to note that the initial rate increased throughout the relevant temperature range instead of passing through a peak value and dropping in the manner of the maximum desulfurization rate. Whereas the maximum rate only doubled between 2100 and 2200°F, the initial rate increased almost six times. The evidence indicates that the initial and maximum rates are probably not determined by the same rate controlling mechanism.

When sulfur dioxide was not present in the gas fed, the results shown in Figure 21 were obtained. With 4 per cent carbon monoxide, the maximum desulfurization rate appeared to be affected by temperature in about the same way as before except that the peak value of the rate was reached at 2150°F, which was about 100°F lower than when sulfur dioxide was fed. With 2 per cent carbon monoxide, the maximum rate was only slightly affected by temperature. Moreover, the rate did not drop off at the upper end of the temperature range as it did in the previous cases. Thus the effect of temperature on the desulfurization rate seemed to vary widely according to the composition of the gas phase.

Although the physical size and shape of the residual solids did not differ noticeably from the untreated gypsum, the surface of the particles did present a different appearance. The raw gypsum had a relatively smooth surface, while the solids recovered from runs carried out in the range of 2100 to 2200°F presented a rough or textured surface and solids which had been heated to around 2300°F had a glassy surface. At the

Figure 20. Effect of temperature on the initial desulfurization rate

gas composition, 4% CO, 10% CO_2, 5% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

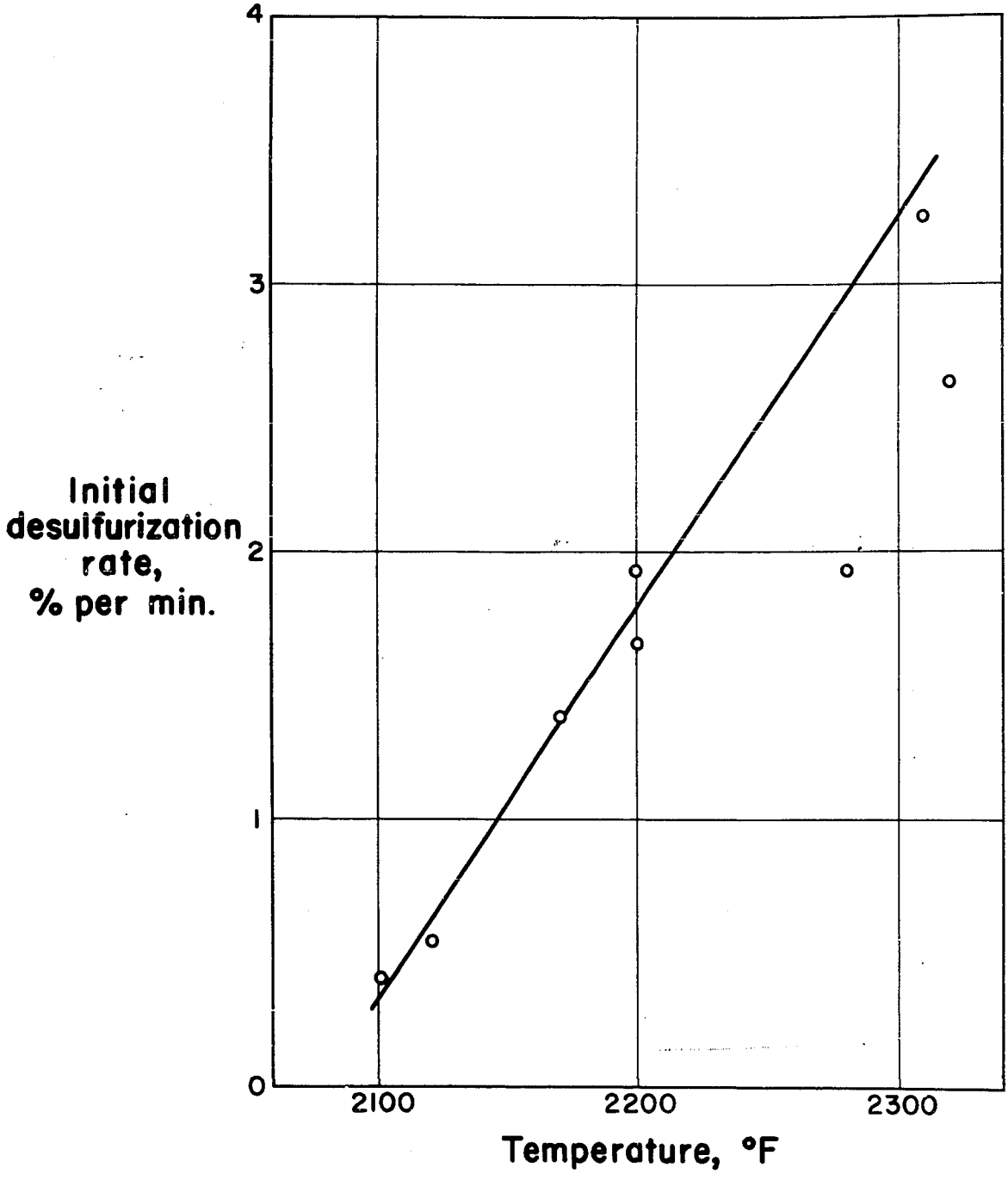
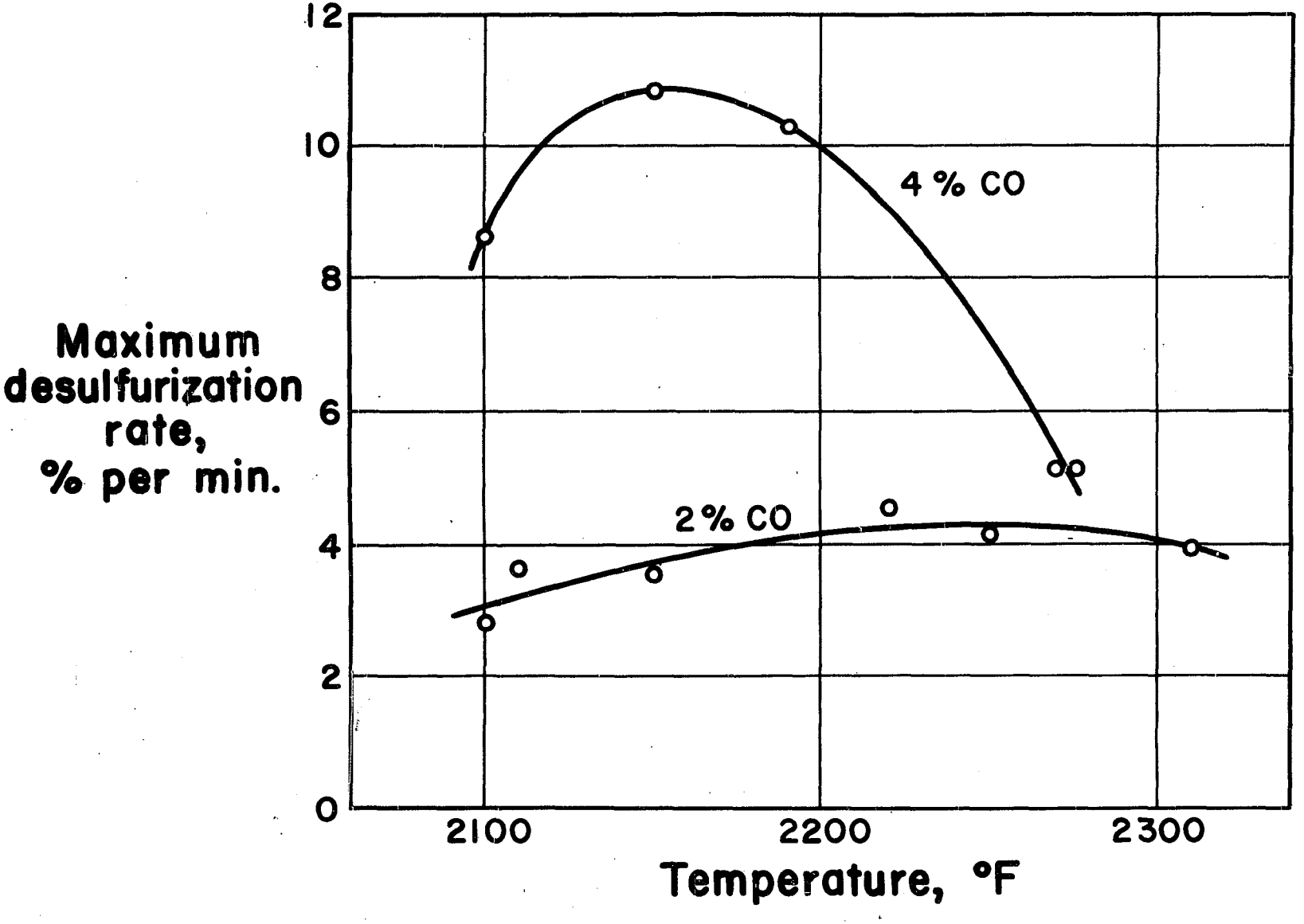

Initial desulfurization rate, % per min.
4
3
2
1
0
2100
2200
2300
Temperature, °F

Figure 21. Effect of temperature on the maximum desulfurization rate

gas composition, 5% CO_2, 0% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Maximum desulfurization rate, % per min.
12
10
8
6
4
2
0
4 % CO
2% CO
2100
2200
2300
Temperature, °F

highest temperature some sintering evidently took place as the residual particles had a tendency to stick together. Photomicrographs of untreated gypsum, solids from a run conducted at 2200 to 2215°F, and solids from a run carried out at 2300 to 2320°F are shown in Figure 22.

The drop in the maximum desulfurization rate which occurred between 2200 and 2300°F could have been due either to a structural change or to incipient fusion of the gypsum. The glassy surface which the particles acquired at the higher temperature would seem likely to seal the pores in the solid and prevent passage of the gaseous reactants and products of reaction. However, a structural change is also known to occur in the range of 2215 to 2245°F (29, 43). This could also affect the reaction equilibrium and rate of decomposition.

Effect of mass velocity The effect of mass velocity on the desulfurization rate was studied using two different gas compositions, a nominal temperature of 2200°F, a single particle size, and a single bed depth. Since the mass velocity varied while the bed depth remained constant, the ratio of charge weight to gas feed rate also varied from run to run. This ratio decreased as the mass velocity was increased.

When the gas fed contained 2 per cent carbon monoxide and 98 per cent nitrogen, the results plotted in Figure 23 were obtained. Using 3 per cent carbon monoxide, 20 per cent carbon dioxide, and 5 per cent sulfur dioxide in the feed yielded the results of Figure 24. In both cases the maximum desulfurization rate increased almost lineally with mass velocity in the range of 0.1 to 0.3 pounds per second per square foot. However, the rate of increase was greater for the first case. The initial desulfurization rate was plotted for the second case and it decreased with mass velocity.

Figure 22. Photomicrographs of -7 +8 mesh particles showing effect of temperature

A. Untreated gypsum

B. Solids from Run 199 carried out at 2200 to 2215°F

C. Solids from Run 198 carried out at 2300 to 2320°F

Figure 23. Effect of mass velocity on the maximum desulfurization rate

gas composition, 2% CO, 0% CO_2, 0% SO_2
temperature, 2220 to 2250°F
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

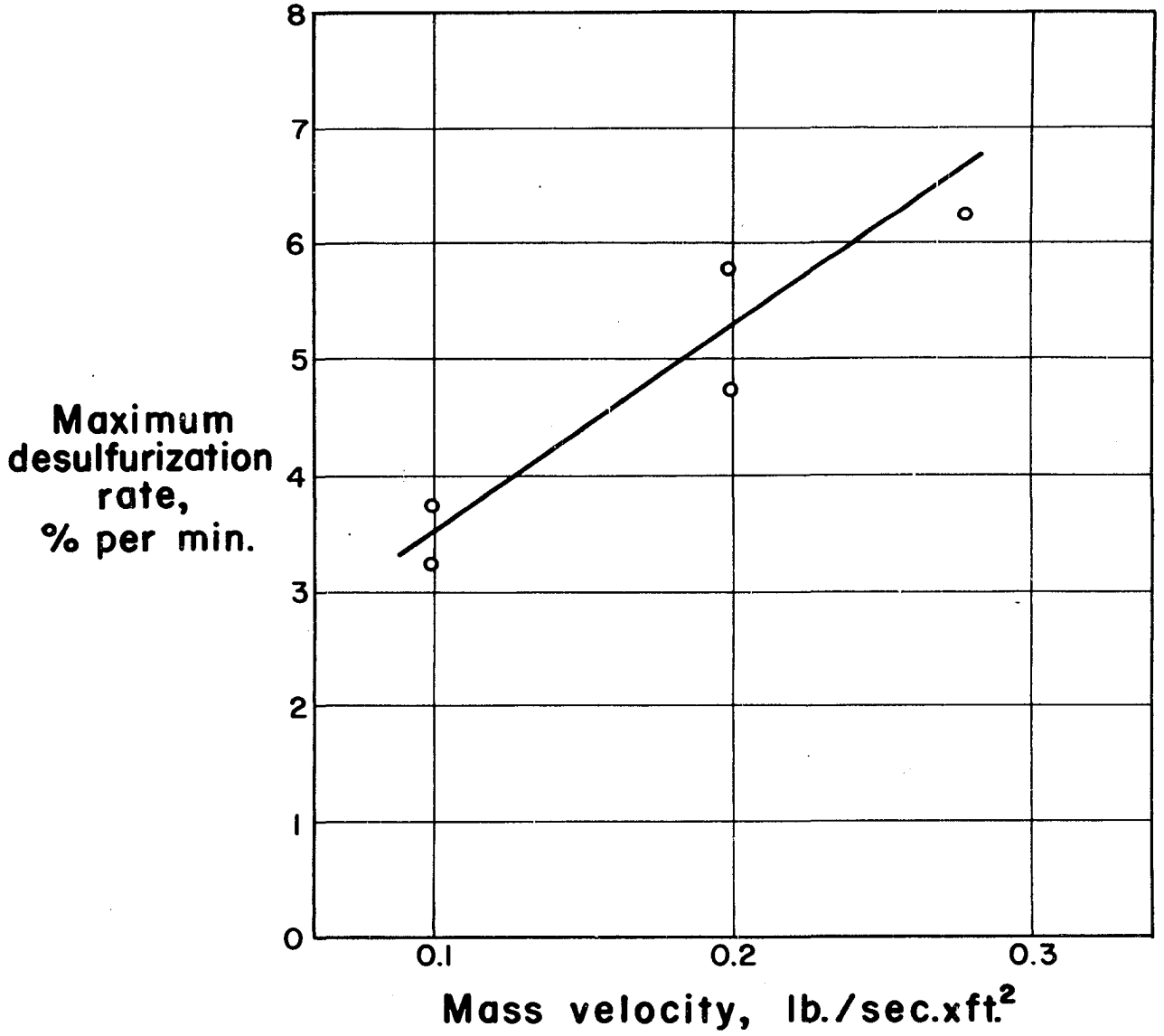
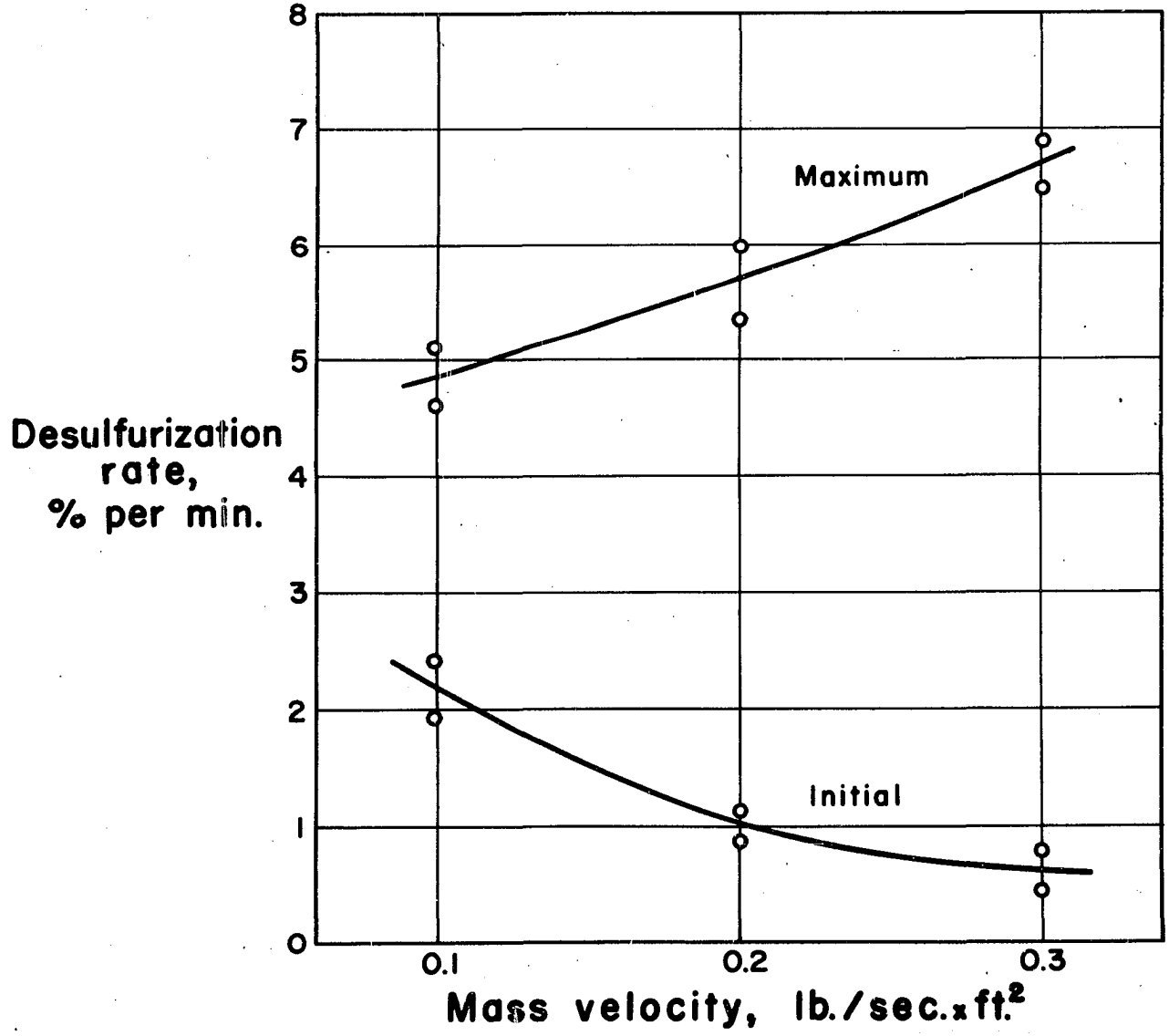

Maximum desulfurization rate, % per min.
0
1
2
3
4
5
6
7
8
0.1
0.2
0.3
Mass velocity, lb./sec.xft.²

Figure 24. Effect of mass velocity on the desulfurization rate

gas composition, 3% CO, 20% CO_2, 5% SO_2
temperature, 2190 to 2220°F
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Desulfurization rate, % per min.
8
7
6
5
4
3
2
1
0
Maximum
Initial
0.1
0.2
0.3
Mass velocity, lb./sec.x ft.²

This was completely unexpected and no logical explanation was apparent.

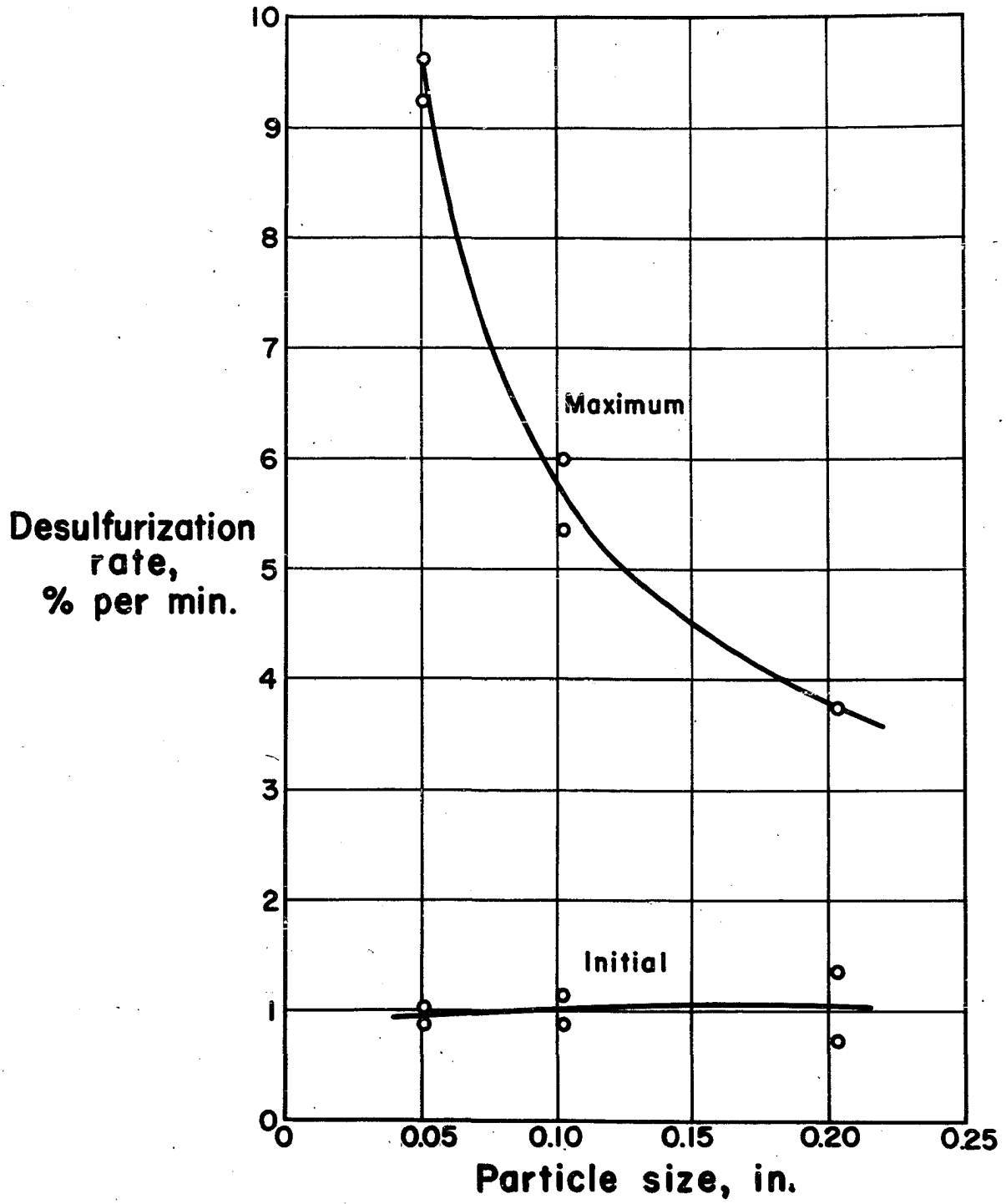
In general the reaction rate should increase with mass velocity when the mass transfer rate is the controlling rate mechanism. But changes in mass velocity also affect the outlet gas composition and hence affect the average concentration of the reactants. In this particular case increasing the mass velocity had the effect of increasing the average carbon monoxide concentration. The latter in turn would have the effect of increasing the maximum desulfurization rate.

It was possible to estimate the change in the average carbon monoxide concentration and thereby to estimate what proportion of the change in the maximum desulfurization rate could be due to this and what proportion could be due to the change in the mass transfer rate. For the results of Figure 23 it was estimated that the increase in average carbon monoxide concentration could account for only 15 per cent of the increase in maximum desulfurization rate. For this set of conditions it would seem that the mass transfer rate is the controlling rate mechanism. However, for Figure 24 the increase in average carbon monoxide concentration could account for 73 per cent of the increase in rate. Consequently, some mechanism other than transport appears to be the dominant rate controlling mechanism.

Effect of particle size Most of the runs were made using -7 +8 mesh particles of gypsum. To determine what effect particle size might have on the desulfurization rate some runs were made using -12 +14 mesh particles and some using -3½ +4 mesh particles. The effect of particle size was investigated for only a single set of conditions. The results appear in Figure 25. In this graph the desulfurization rate is

Figure 25. Effect of particle size on the desulfurization rate of gypsum

gas composition, 3% CO, 20% CO_2, 5% SO_2
temperature, 2160 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
bed depth, 1.0 in.


Desulfurization rate, % per min.
10
9
8
7
6
5
4
3
2
1
0
Maximum
Initial
0
0.05
0.10
0.15
0.20
0.25
Particle size, in.

plotted against particle size determined as the average screen opening.

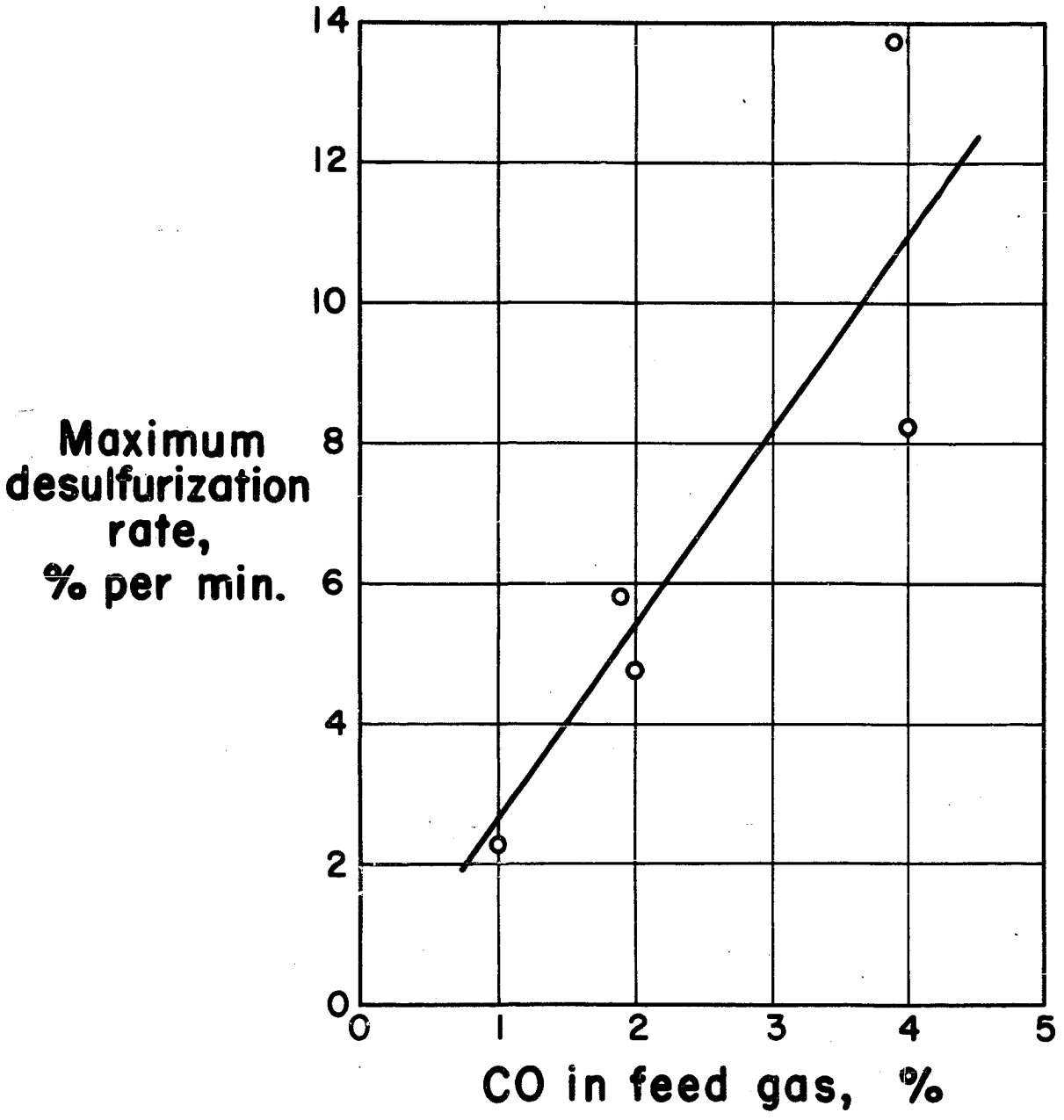
For the given conditions the initial desulfurization rate was almost completely independent of particle size, but the maximum desulfurization rate was found to decrease rapidly as the particle size increased.

In general, the reaction rate could decrease as the particle diameter increases because (1) the outside surface area per unit volume decreases, (2) the resistance to diffusion across the external gas film increases, or (3) the length of the mean diffusion path through the internal pores increases. The first can probably be ruled out because the outside surface area of the particles is probably small compared to the total surface area. The second is also probably not a factor since it was pointed out in the previous section that the mass transfer rate did not seem to be the controlling rate mechanism for this particular set of conditions. Therefore the rate of internal diffusion would seem most likely to be rate controlling. The mechanism which controls the initial desulfurization rate must be entirely different since the rate was not affected by particle size.

Effect of carbon monoxide In order to determine what effect the carbon monoxide concentration might have, a series of runs was carried out in which the concentration of this reactant was varied while all other conditions were kept constant. This was repeated for three different combinations of carbon dioxide and sulfur dioxide concentrations. The first combination involved a feed gas containing no carbon dioxide or sulfur dioxide. The results are presented in Figure 26. As shown, the maximum desulfurization rate increased with carbon monoxide concentration. The data points were badly scattered at the highest concentration which may

Figure 26. Effect of carbon monoxide on the maximum desulfurization rate

gas composition, 0% CO_2, 0% SO_2
temperature, 2210 to 2250°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


Maximum desulfurization rate, % per min.
14
12
10
8
6
4
2
0
0
1
2
3
4
5
CO in feed gas, %

have been a result of the formation of considerable calcium sulfide in the product.

When 5 per cent carbon dioxide was included in the feed gas, the results of Figure 27 were obtained. The points representing the maximum desulfurization rate for various levels of carbon monoxide fell fairly close to a straight line. There was little or no calcium sulfide in the product of these runs. A straight line plotted through the points had a slope only slightly less than the corresponding line for Figure 26. The addition of carbon dioxide then seemed to have only a small effect on the desulfurization rate but a large effect on the amount of calcium sulfide produced.

The third series of runs was made with a feed gas containing 20 per cent carbon dioxide and 5 per cent sulfur dioxide, in addition to carbon monoxide and nitrogen. The desulfurization curves were "S" shaped, so there was a large difference between the initial and maximum desulfurization rates. Figure 28 shows the desulfurization rate as a function of the carbon monoxide concentration. Both the initial and maximum rates appeared to increase lineally with reactant concentration. At the higher concentrations some falling off in the maximum rate was observed and this may have been due to the formation of calcium sulfide. Little or no sulfide was found in the product of runs made with 5 per cent carbon monoxide or less. For this set of conditions 2 per cent carbon monoxide seems to be about the minimum concentration which will give a desulfurization rate large enough to consider.

Effect of carbon dioxide The effect of carbon dioxide concentration on desulfurization rate was examined using several combinations

Figure 27. Effect of carbon monoxide on the maximum desulfurization rate

gas composition, 5% CO_2, 0% SO_2
temperature, 2190 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

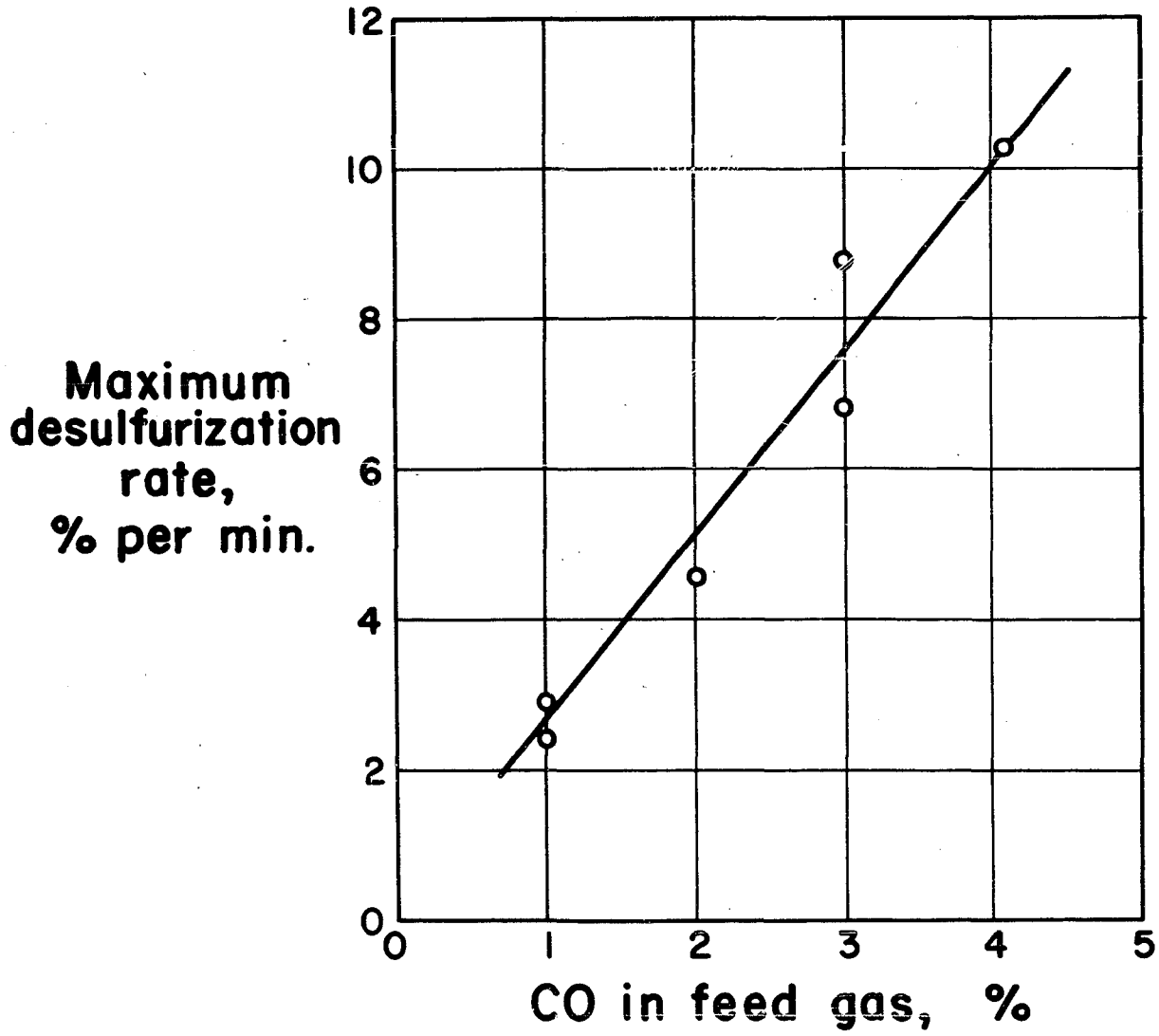
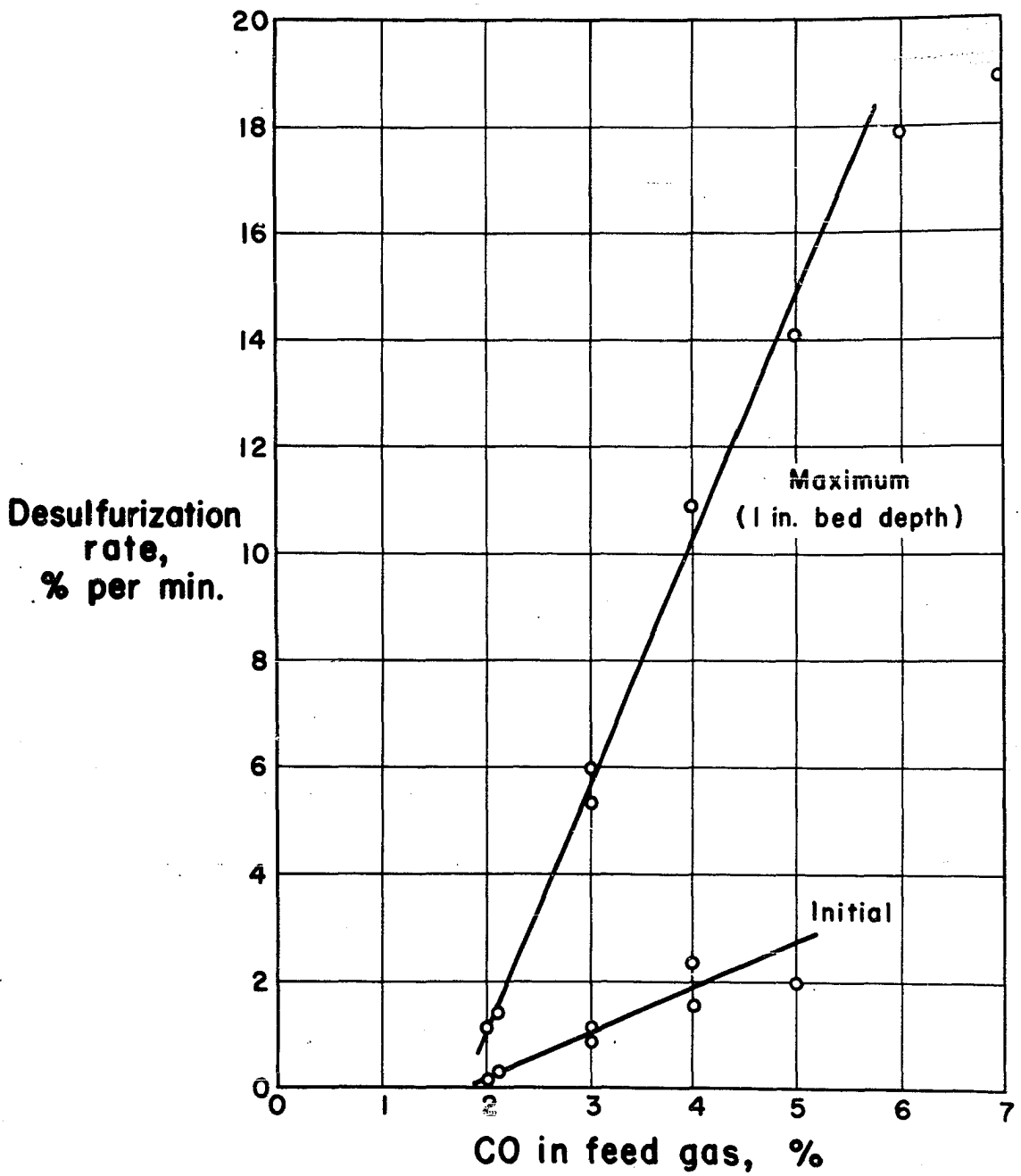

Maximum desulfurization rate, % per min.
12
10
8
6
4
2
0
0
1
2
3
4
5
CO in feed gas, %

Figure 28. Effect of carbon monoxide on the desulfurization rate

gas composition, 20% CO_2, 5% SO_2
temperature, 2140 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh


Desulfurization rate, % per min.
20
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
Maximum
(1 in. bed depth)
Initial
CO in feed gas, %

of carbon monoxide and sulfur dioxide concentrations and constant values of nominal temperature, mass velocity, and particle size.

To begin with, a feed gas containing 2 per cent carbon monoxide and 0 per cent sulfur dioxide was used. The values of the maximum desulfurization rates which were observed are plotted as a function of the carbon dioxide concentration in the feed gas in Figure 29. The maximum desulfurization rate appeared to decrease as the carbon dioxide concentration was increased from 0 to 10 per cent, but increasing the concentration further to 15 per cent seemed to have little effect.

When the feed gas contained 5 per cent sulfur dioxide and various levels of carbon monoxide, the results given in Figure 30 were obtained. At the 3 and 5 per cent carbon monoxide levels the relationship between maximum desulfurization rate and carbon dioxide concentration was similar to that previously noted in Figure 29. That is, the rate decreased with increasing amounts of carbon dioxide, rapidly at first and then leveling out as the concentration increased further. At the 5 per cent carbon monoxide level large amounts of calcium sulfide were produced when less than 20 per cent carbon dioxide was used, so it did not seem practical to attempt measurement of desulfurization rates for low concentrations of carbon dioxide. The results for the 4 per cent carbon monoxide level were anomalous in that the maximum desulfurization rate appeared to increase with carbon dioxide concentration, pass through a maximum, and then decrease. This may have been due in part to the formation of considerable calcium sulfide when the feed contained 5 per cent carbon dioxide. However, the results were scattered so that it is not possible to infer what the exact relationship is.

Figure 29. Effect of carbon dioxide on the maximum desulfurization rate

gas composition, 2% CO, 0% SO_2
temperature, 2190 to 2230°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

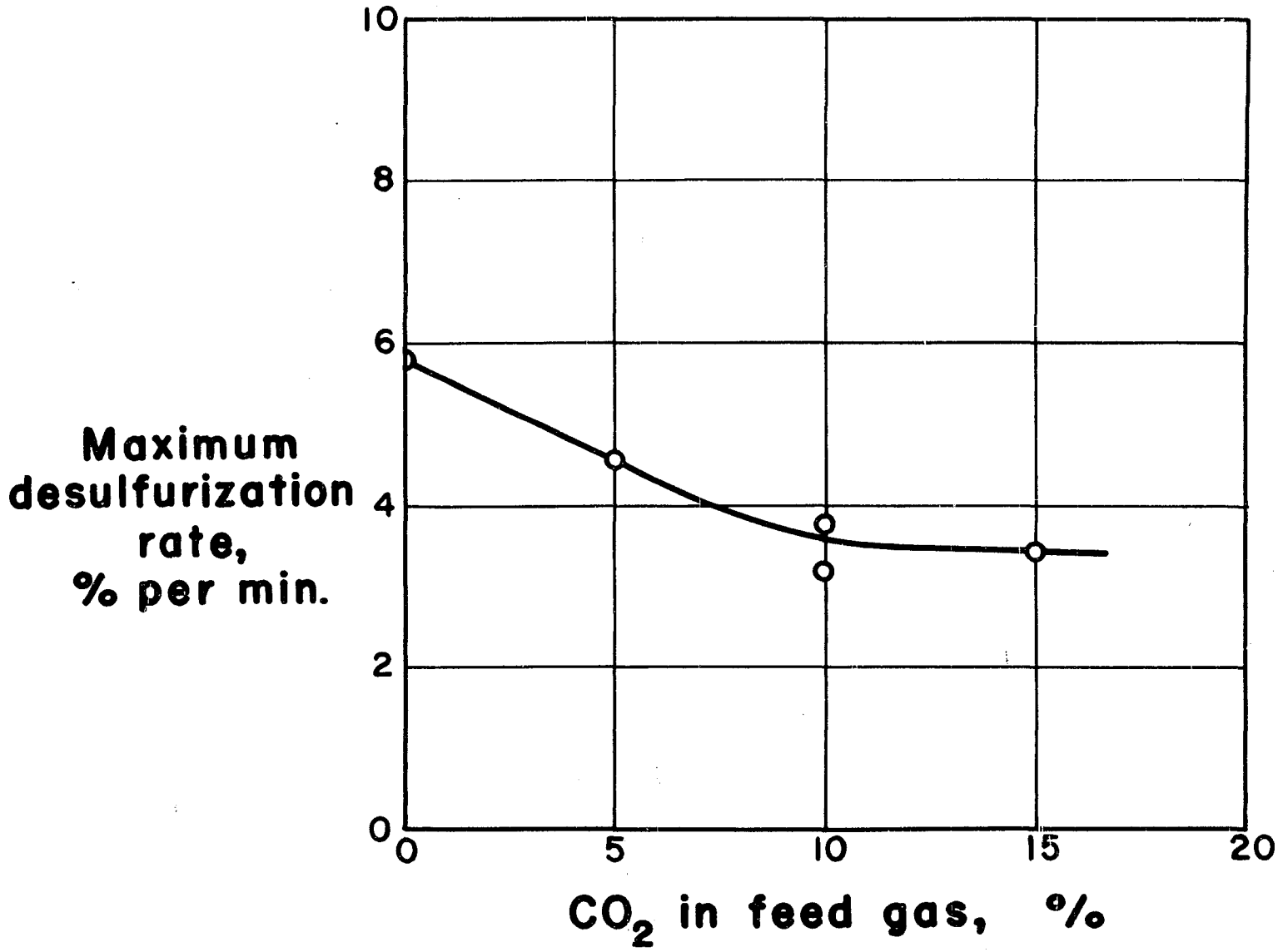
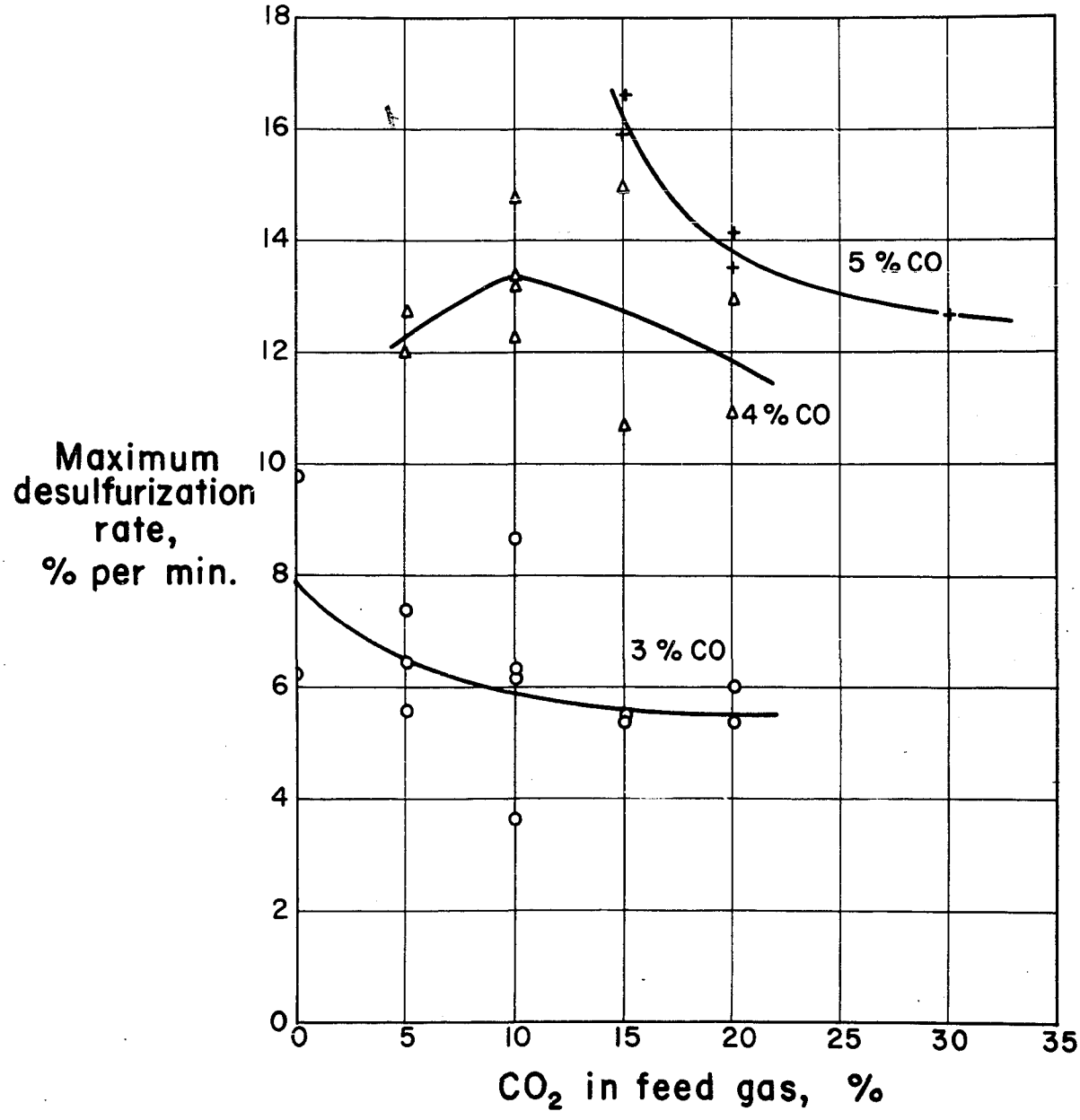

Maximum desulfurization rate, % per min.
10
8
6
4
2
0
0
5
10
15
20
CO_2 in feed gas, %

Figure 30. Effect of carbon dioxide on the maximum desulfurization rate

gas composition, 5% SO_2
temperature, 2140 to 2210°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh


Maximum desulfurization rate, % per min.
18
16
14
12
10
8
6
4
2
0
0
5
10
15
20
25
30
35
5 % CO
4 % CO
3 % CO
CO_2 in feed gas, %

An attempt to correlate the initial desulfurization rate with carbon dioxide concentration was not successful. Even the best results, which are plotted in Figure 31, were widely scattered. About the only inference which can be made is that the initial desulfurization rate appears to increase somewhat with carbon dioxide concentration for the particular set of conditions used.

Effect of sulfur dioxide The effect of sulfur dioxide concentration was determined at three different levels of carbon monoxide concentration but for only single levels of carbon dioxide concentration, nominal temperature, mass velocity and particle size. The resulting maximum desulfurization rates are shown as a function of sulfur dioxide concentration in Figure 32. Widely varying results were obtained. At the 2 per cent carbon monoxide level the maximum desulfurization rate decreased as the sulfur dioxide concentration was increased from 0 to 0.5 per cent but then the rate increased slightly as the sulfur dioxide concentration was increased. The effect was just the opposite at the 3 per cent carbon monoxide level. Here the rate increased at first and then decreased at higher concentrations of sulfur dioxide. Still a different effect was observed at the 4 per cent carbon monoxide level. Although the results were scattered, the maximum desulfurization rate seemed to increase slightly with sulfur dioxide concentration throughout the range investigated.

A small amount of sulfur dioxide in the feed gas had a very noticeable effect on the initial desulfurization rate. When sulfur dioxide was fed, the maximum desulfurization rate was attained almost immediately. On the other hand, the inclusion of only 0.5 per cent sulfur dioxide in the feed (at the 2 per cent carbon monoxide level) caused the initial rate to be

Figure 31. Effect of carbon dioxide on the initial desulfurization rate

gas composition, 3% CO, 5% SO_2
temperature, 2200 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

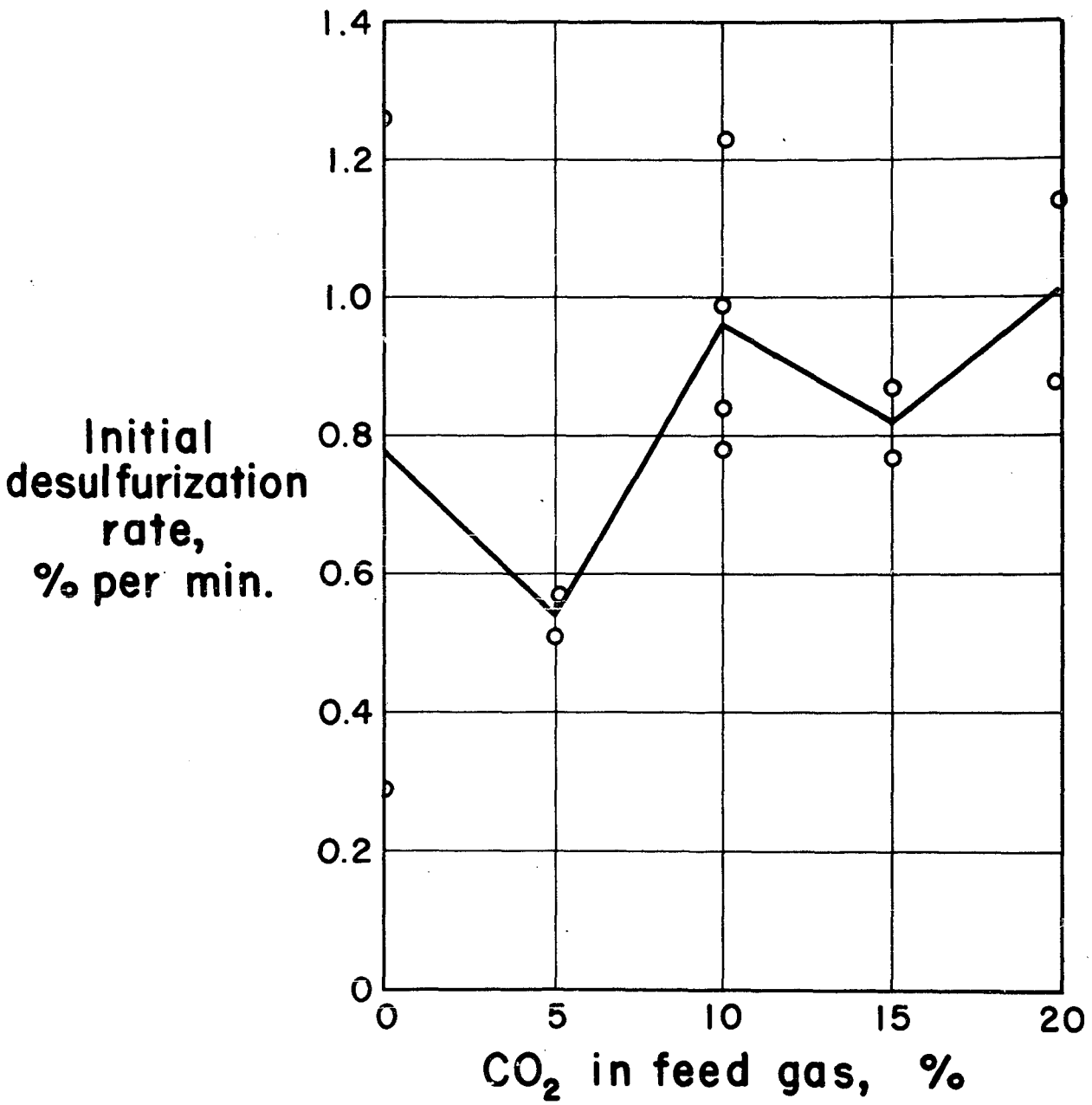
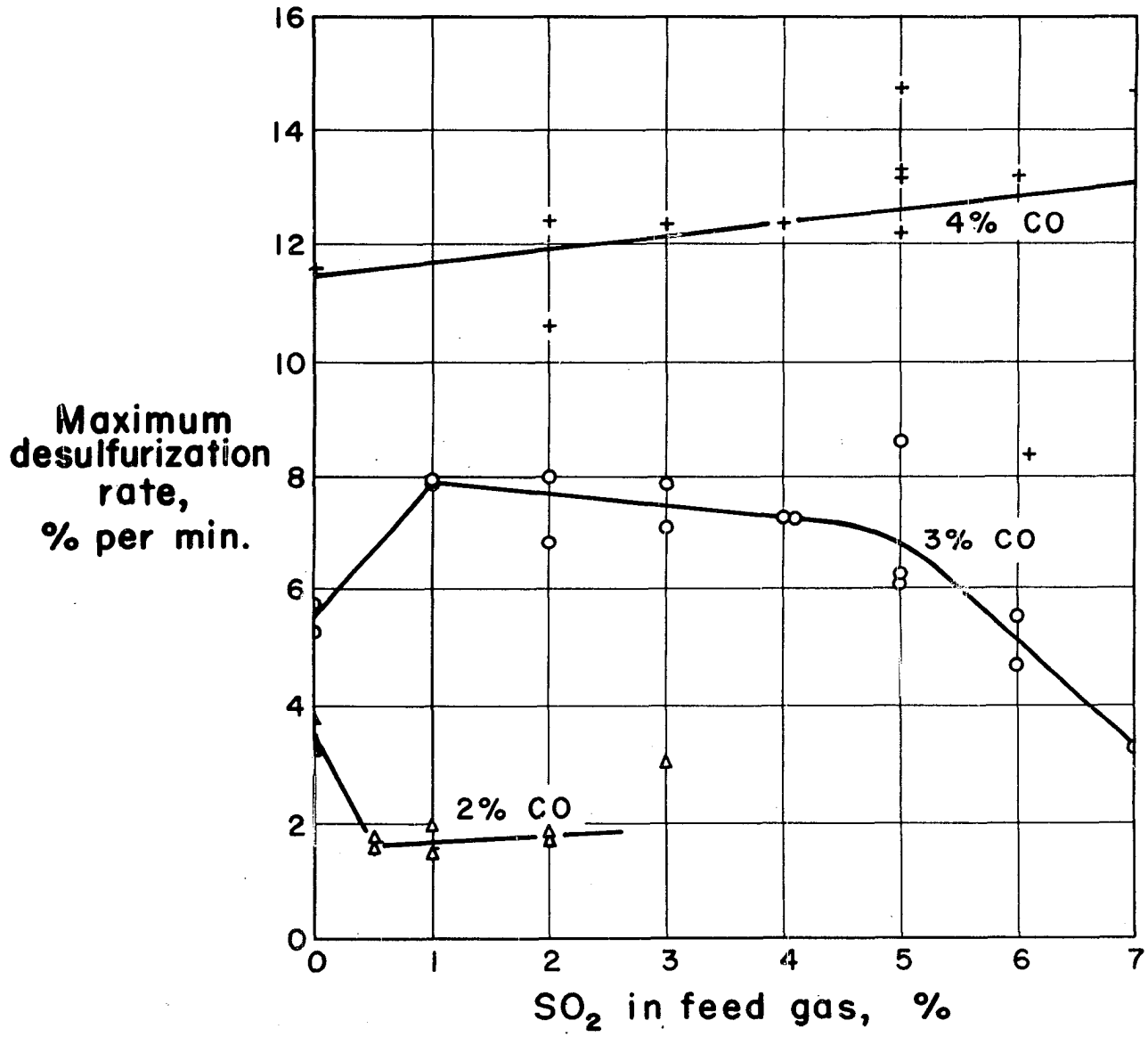

Initial desulfurization rate, % per min.
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0
0
5
10
15
20
CO_2 in feed gas, %

Figure 32. Effect of sulfur dioxide on the maximum desulfurization rate

gas composition, 10% CO_2
temperature, 2140 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh


Maximum desulfurization rate, % per min.
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
4% CO
3% CO
2% CO
SO2 in feed gas, %

measurably less than the maximum rate. The effect of sulfur dioxide concentration on the initial rate is shown by Figure 33. Increasing the sulfur dioxide concentration from 0 to 2 per cent resulted in the sharpest reduction in the initial desulfurization rate. Although the results for the 4 per cent carbon monoxide level were not included in the diagram, they were similar in nature to the other levels but more scattered.

Calculated conversion of carbon monoxide For any given desulfurization rate it is possible to calculate the conversion of carbon monoxide per pass through the reactor. The principal assumption which has to be made is that calcium sulfate and carbon monoxide react according to Reaction 2. The conversion calculated in this manner is not the total conversion since it does not include the conversion of carbon monoxide by side reactions such as Reaction 4. No attempt was made to estimate the total conversion.

The most interesting result was obtained when the conversions calculated for the maximum desulfurization rates of Figure 28 were plotted against the carbon monoxide concentration, giving the curve shown in Figure 34. The conversion increased rapidly as the carbon monoxide concentration was increased to 3.5 per cent, but beyond this point it seemed to be independent of reactant concentration. For this series of runs the feed gas contained 20 per cent carbon dioxide and 5 per cent sulfur dioxide. When the concentration of carbon dioxide was reduced and the sulfur dioxide was omitted, the conversion of carbon monoxide seemed to be independent of carbon monoxide concentration even at low concentrations. This conclusion can be drawn from the values presented in Table 6. The conversions in Table 6 were based on the maximum desulfurization rates

Figure 33. Effect of sulfur dioxide on the initial desulfurization rate

gas composition, 10% CO_2
temperature, 2190 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

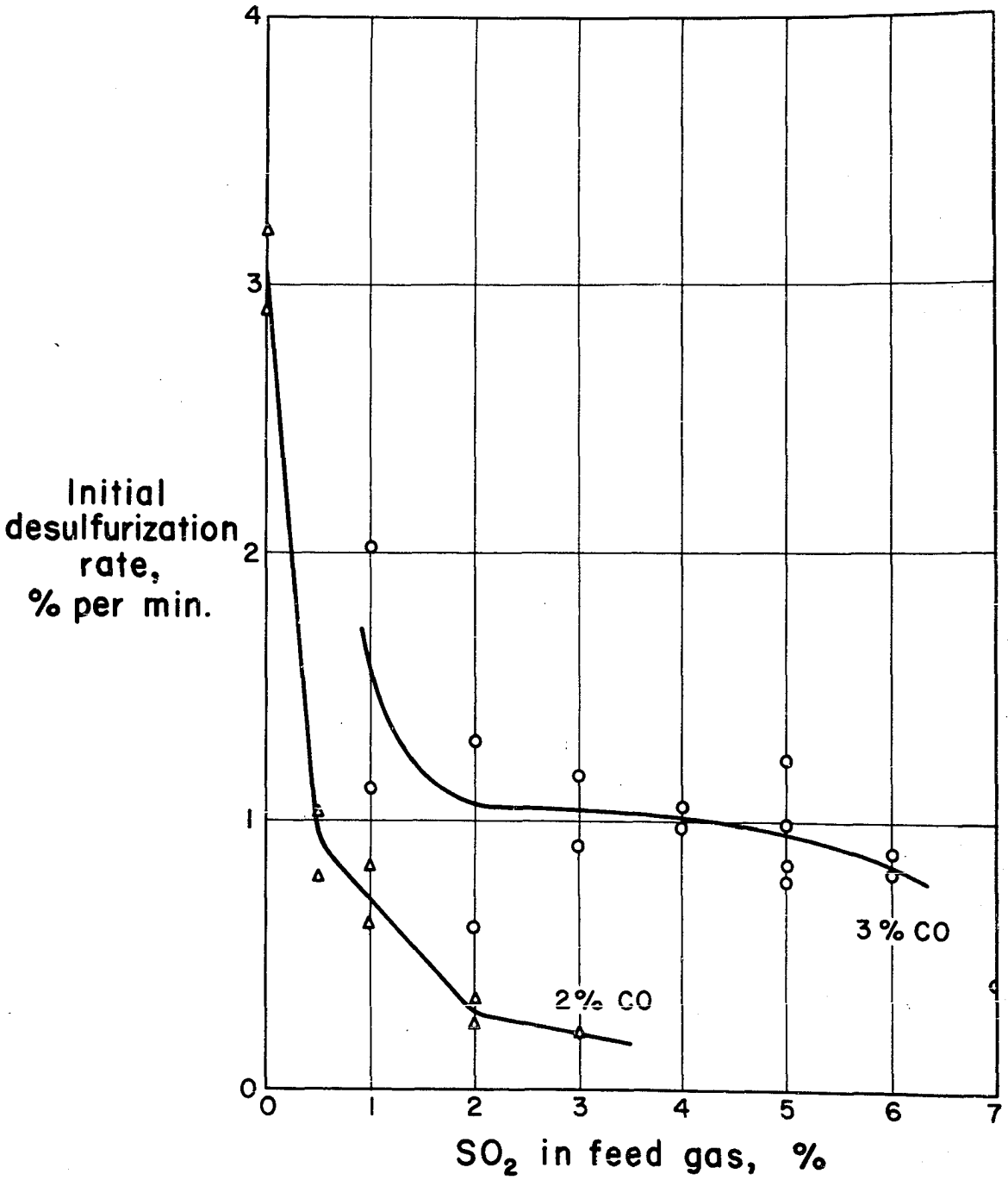

Initial desulfurization rate, % per min.
4
3
2
1
0
0
1
2
3
4
5
6
7
3% CO
2% CO
SO2 in feed gas, %

Figure 34. Effect of carbon monoxide concentration on the estimated conversion of carbon monoxide

gas composition, 20% CO_2, 5% SO_2
temperature, 2140 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.

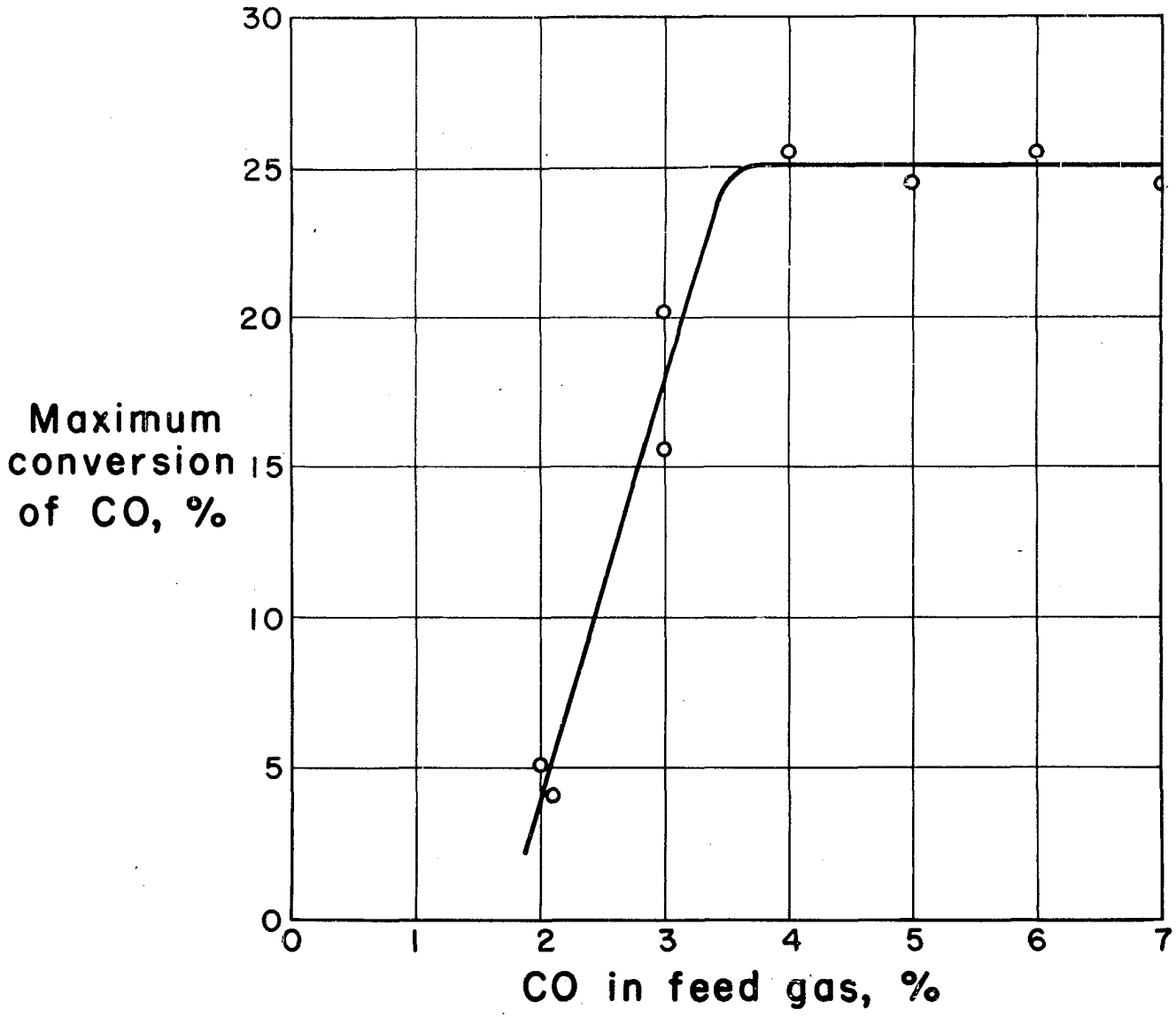

Maximum conversion of CO, %
30
25
20
15
10
5
0
0
1
2
3
4
5
6
7
CO in feed gas, %

Table 6. Calculated maximum conversion of carbon monoxide by the desulfurization reaction

(5% CO_2, 0% SO_2, -7 +8 mesh gypsum, mass velocity = 0.2 lb./sec. x $ft.^2$)

Run no.	CO in feed, %	Temp. °F	Conversion of CO, %
61	1.0	2210	22.0
170	1.0	2220	19.8
62	2.0	2220	17.3
63	3.0	2200	17.5
107	3.0	2200	22.1
64	4.1	2190	21.6

plotted in Figure 27.

For both series of runs mentioned above the ratio of charge weight to feed gas rate was nearly constant. The only apparent explanation for the sharp break observed in Figure 34 is that the same rate controlling mechanism does not apply throughout the range of carbon monoxide concentration when 20 per cent carbon dioxide and 5 per cent sulfur dioxide are present.

Correlation of calcium sulfide Since an object of the investigation was to find methods for reducing the percentage of calcium sulfide in the lime by-product, the effects of various temperature levels and gas compositions on the side conversion of gypsum to calcium sulfide were studied. The conversion was approximately proportional to the per cent

calcium sulfide in the residual solids, so instead of correlating conversion with operating conditions, the per cent of calcium sulfide was correlated.

In order to limit the scope of the study the effects of mass velocity and particle size were not examined.

Effect of temperature The effect of temperature on calcium sulfide formation was explored in the range of 2100 to 2310°F for single values of mass velocity and particle size at various gas feed compositions. In general an attempt was made to correlate the per cent of calcium sulfide in the by-product with the average bed outlet temperature during the maximum desulfurization rate period. Hence the implicit assumption was made that the rate of formation of calcium sulfide is proportional to the desulfurization rate.

For the case where the feed gas contained 4 per cent carbon monoxide, 10 per cent carbon dioxide, and 5 per cent sulfur dioxide the effect of temperature on the per cent of calcium sulfide occurring in the residual solids is graphically illustrated in Figure 35. With this set of conditions, a very large amount of calcium sulfide was produced at 2100°F but the amount decreased rapidly as the temperature was increased to 2200°F. Further increasing the temperature to 2300°F seemed to have little effect on the amount of calcium sulfide.

The effect of temperature when other gas compositions were used is indicated in Table 7. Here again the by-product contained relatively large amounts of calcium sulfide when the runs were carried out at 2100°F. But for temperatures in the range of 2200 to 2300°F, no calcium sulfide was found in the solids.

Figure 35. Effect of temperature on the per cent of calcium sulfide in the by-product

gas composition, 4% CO, 10% CO_2, 5% SO_2
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

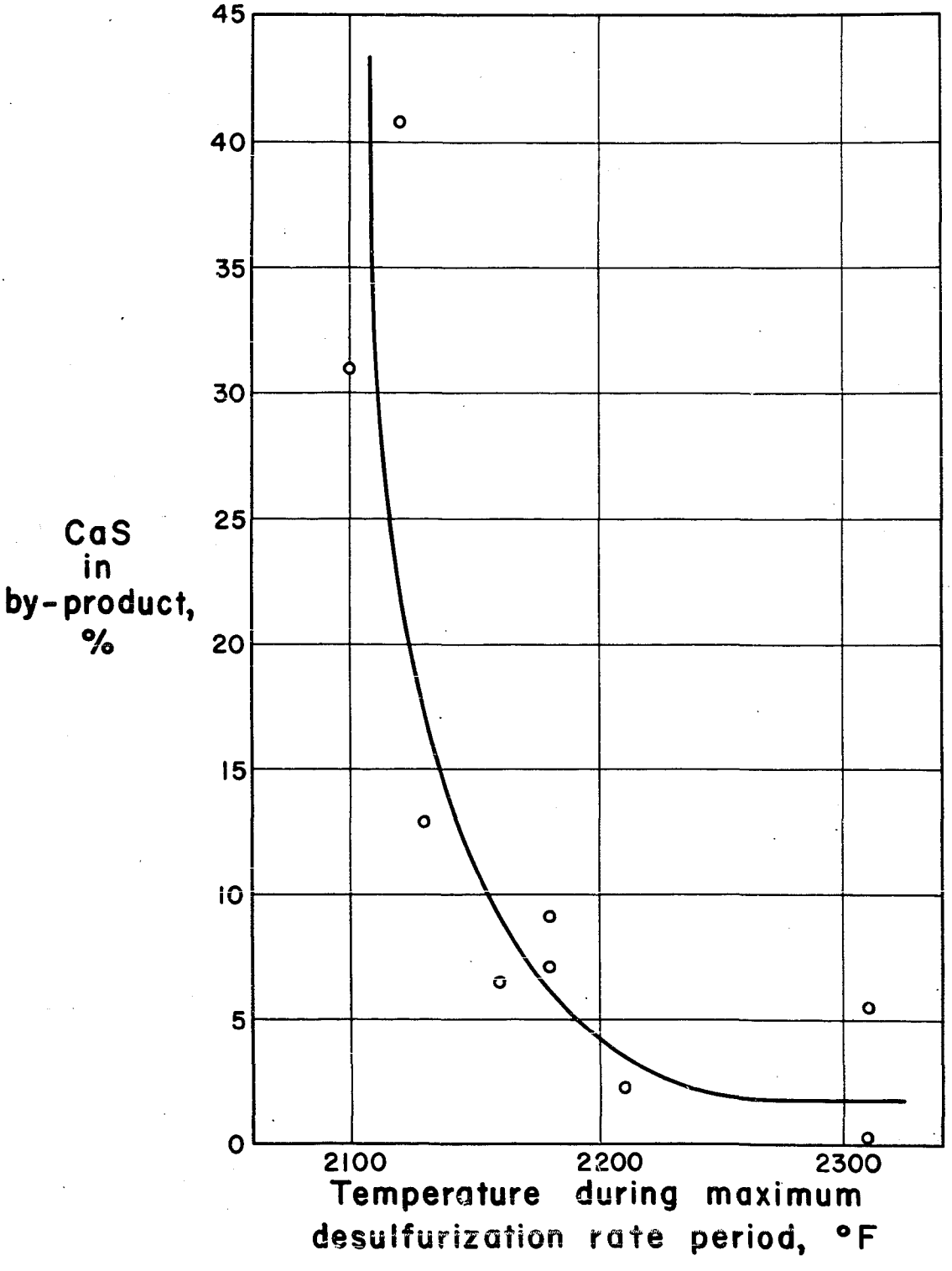

45
40
35
30
25
20
15
10
5
0
CaS in by-product, %
2100
2200
2300
Temperature during maximum desulfurization rate period, °F

Table 7. Effect of temperature on the per cent of calcium sulfide in the by-product

(-7 +8 mesh gypsum, mass velocity = 0.20 lb./sec. x ft.^{2})

Run no.	Gas composition, mole %[a]			Temp.[b] °F	CaS %
	CO	CO_2	SO_2		
76	4.0	5.0	0	2100	24.9
94	4.0	5.1	0	2150	1.1
64	4.1	5.1	0	2190	0
78	4.0	5.0	0	2270	0
91	4.0	5.1	0	2270	0
197	3.0	19.9	5.0	2110	11.2
202	3.0	19.9	5.0	2100	11.2
117	3.0	19.9	5.0	2200	0
193	3.0	19.8	5.0	2190	0
198	3.0	19.9	5.0	2310[c]	0
207	3.0	19.9	5.0	2310[c]	0

[a]Remainder nitrogen.

[b]Mean outlet temp. during max. desulfurization rate period.

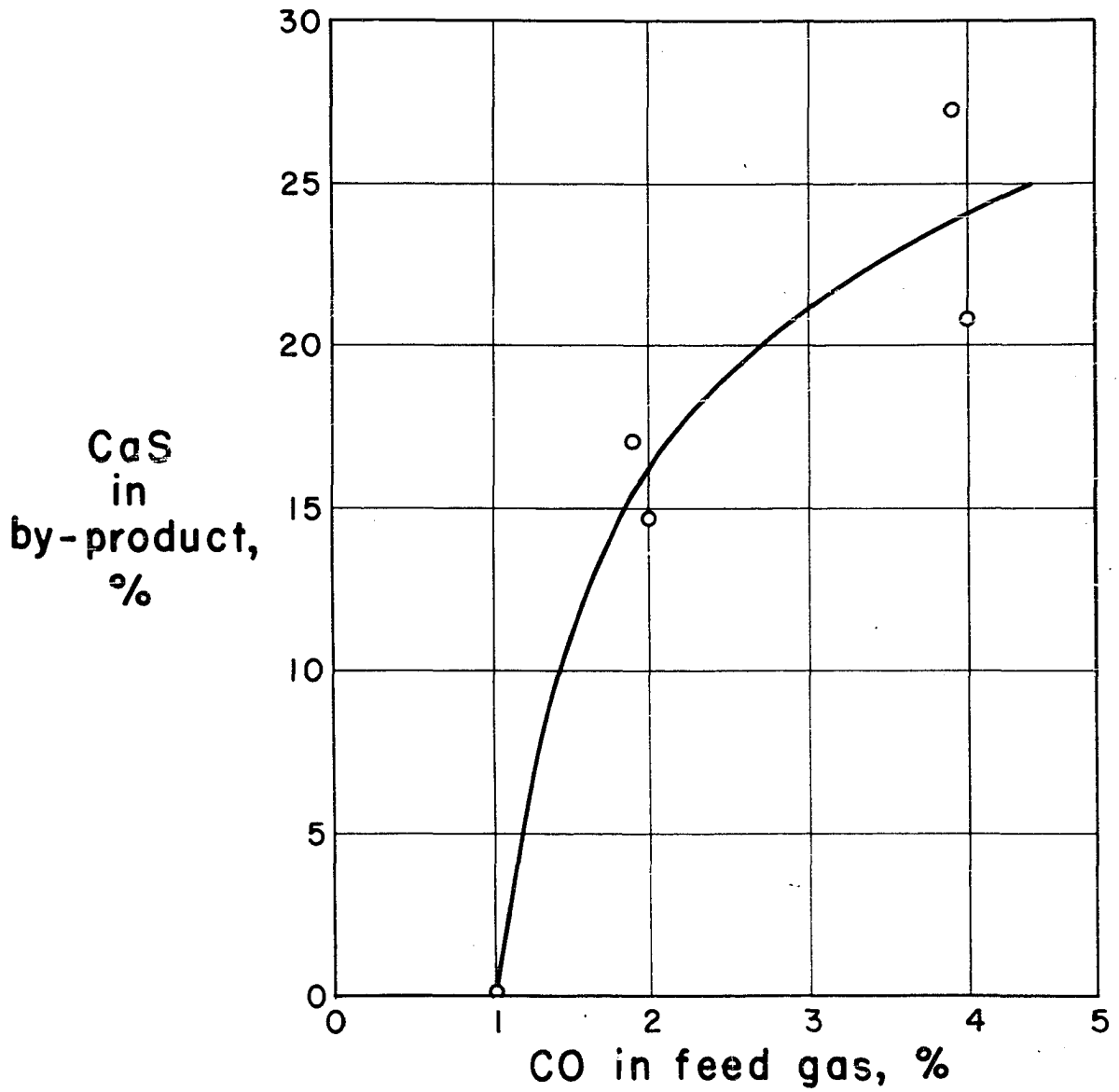
[c]Mean outlet temp. during entire run.

From the standpoint of minimizing the production of calcium sulfide, it appears that the decomposition of gypsum should be carried out at a temperature of 2200°F or higher.

Effect of carbon monoxide The effect of carbon monoxide concentration in the feed gas on the amount of calcium sulfide in the by-product was investigated at a nominal temperature of 2200°F for single values of mass velocity and particle size at several different levels of carbon dioxide and sulfur dioxide. When the feed gas contained only carbon monoxide and nitrogen, the results given in Figure 36 were obtained.

Figure 36. Effect of carbon monoxide on the per cent of calcium sulfide in the by-product

gas composition, 0% CO_2, 0% SO_2
temperature, 2210 to 2250°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh
bed depth, 1.0 in.


CaS
in
by-product,
%
30
25
20
15
10
5
0
0
1
2
3
4
5
CO in feed gas, %

This showed that in the range of 1 to 4 per cent carbon monoxide the per cent of calcium sulfide increased from 0.1 to 24 per cent of the residual solids.

When the feed gas contained 5 per cent sulfur dioxide and various levels of the other components, the results presented in Figure 37 were obtained. Although the data showed considerable variability, certain pronounced trends were apparent. Thus at all levels of carbon dioxide there was a sharp increase in the amount of calcium sulfide produced when the carbon monoxide concentration exceeded 4 per cent. At the 15 and 20 per cent carbon dioxide levels, no calcium sulfide was formed with 3 per cent carbon monoxide. Moreover this was a minimum point on the curve representing 20 per cent carbon dioxide in the feed, as the per cent of calcium sulfide increased for either smaller or larger values of carbon monoxide.

The relatively large variation in the data was probably due to the variation in the control and measurement of temperature.

Effect of carbon dioxide The effect of carbon dioxide in the feed gas on the amount of calcium sulfide left in the by-product was investigated at a nominal temperature of 2200°F for single values of mass velocity and particle size, for several levels of carbon monoxide concentration and for two levels of sulfur dioxide. The results for the case where no sulfur dioxide was present in the feed gas are given in Table 8. At the 1 per cent carbon monoxide level very little calcium sulfide was observed, regardless of whether or not carbon dioxide was present. At higher levels of carbon monoxide the effect of carbon dioxide was very pronounced. Thus when 2 per cent carbon monoxide was fed, two runs

Figure 37. Effect of carbon monoxide on the per cent of calcium sulfide in the by-product

gas composition, 5% SO_2
temperature, 2140 to 2210°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

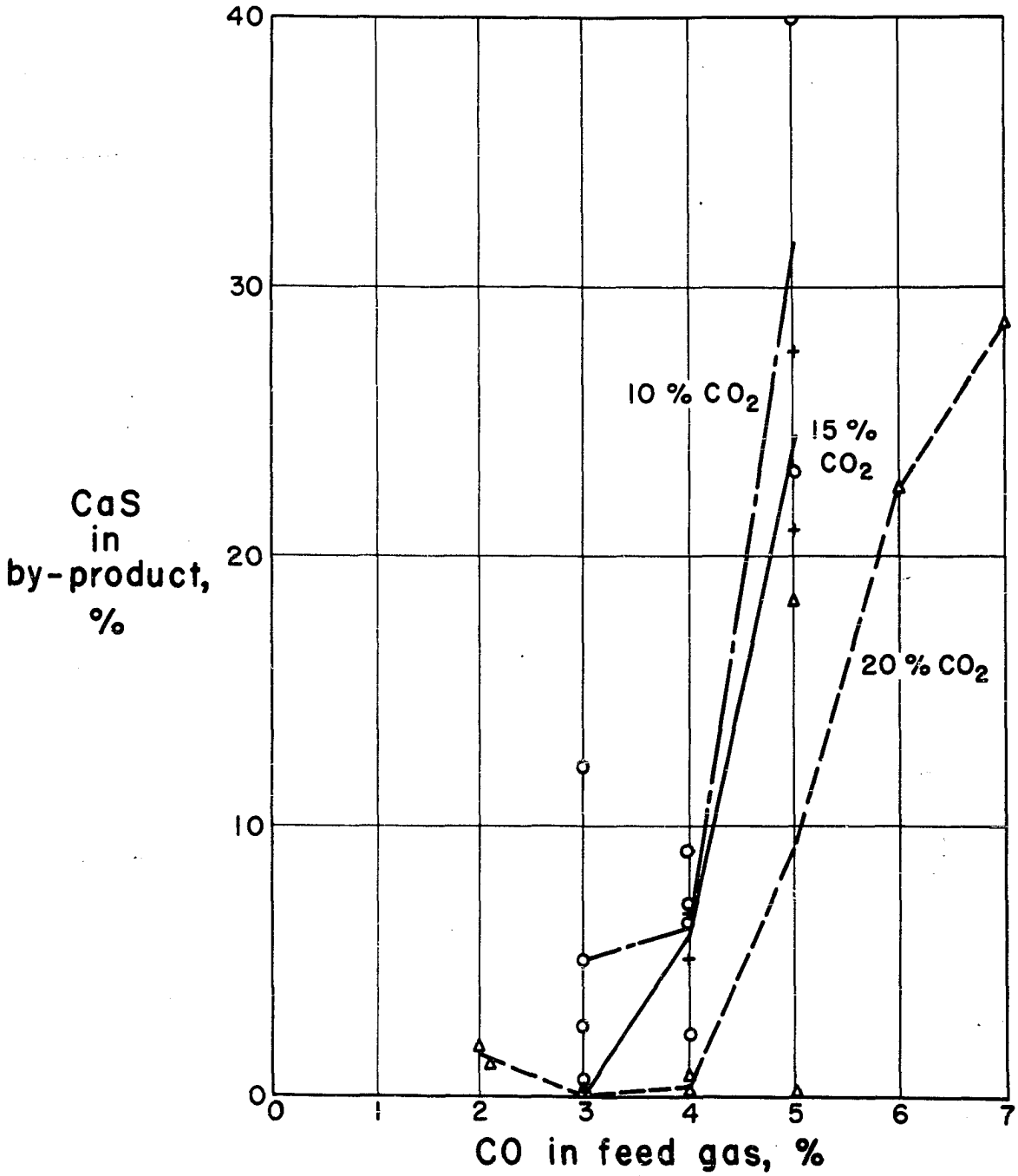

CaS in by-product, %
40
30
20
10
0
0
1
2
3
4
5
6
7
CO in feed gas, %
10 % CO2
15 % CO2
20 % CO2

Table 8. Effect of carbon dioxide on the per cent of calcium sulfide in the by-product

(-7 +8 mesh gypsum, mass velocity = 0.20 lb./sec. x ft.^{2})

Run no.	Gas composition, mole %[a]			Temp.[b] °F	CaS %
	CO	CO_2	SO_2		
51	1.0	0	0	2250	0.1
61	1.0	5.0	0	2210	0
170	1.0	5.0	0	2220	1.2
49	2.0	0	0	2250	14.7
56	1.9	0	0	2230	17.0
62	2.0	5.0	0	2220	0
48	3.9	0	0	2210	27.2
60	4.0	0	0	2220	20.8
64	4.1	5.1	0	2190	0

[a]Remainder nitrogen.

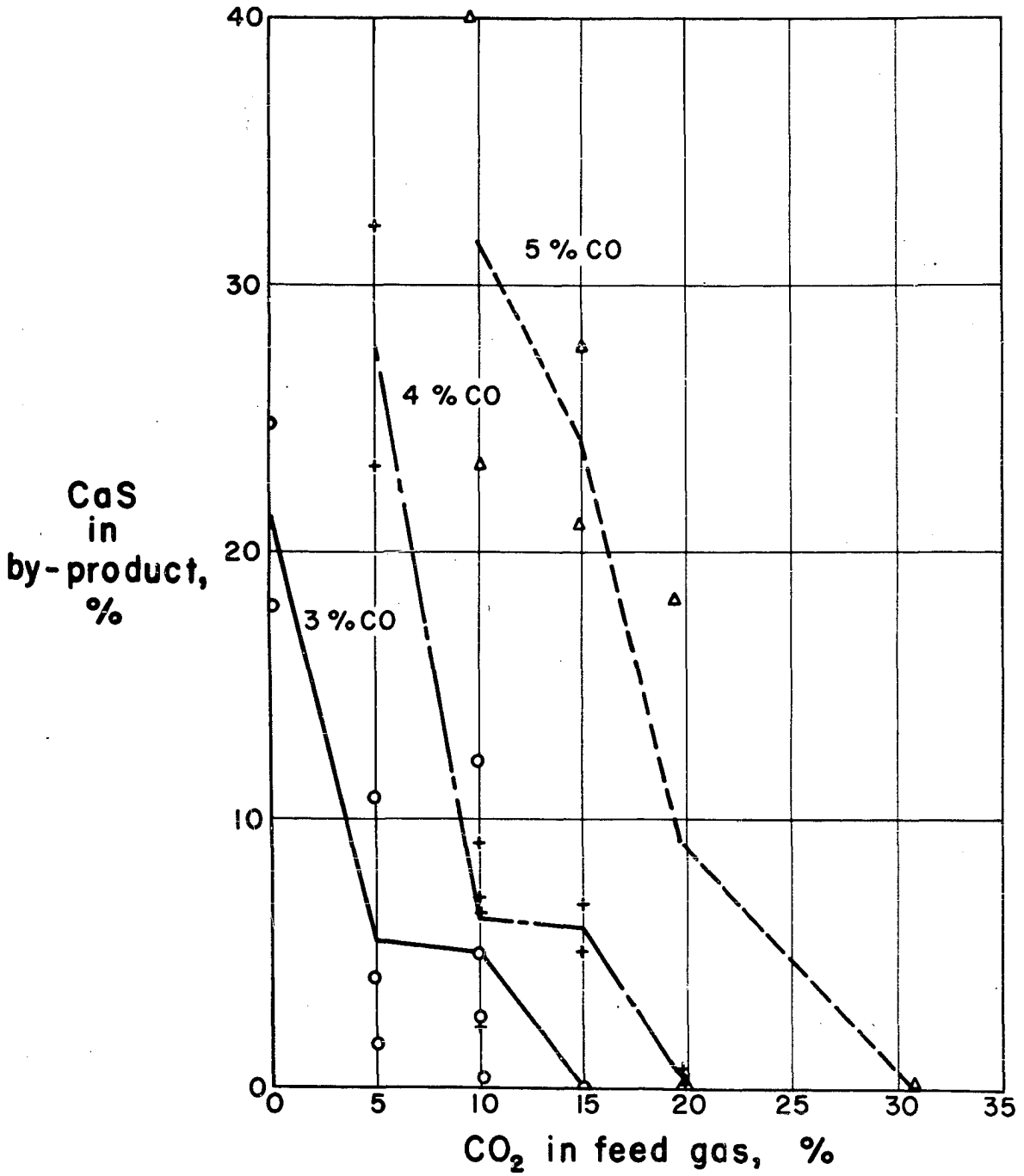
[b]Mean outlet temp. during max. desulfurization rate period.

yielded an average of 16 per cent calcium sulfide, but when only 5 per cent carbon dioxide was added to the feed, no calcium sulfide was found in the product. With 4 per cent carbon monoxide the addition of 5 per cent carbon dioxide caused the calcium sulfide to drop from an average of 24 per cent to 0 per cent.

When 5 per cent sulfur dioxide was present in the feed, the results shown in Figure 38 were obtained. Increasing the per cent of carbon dioxide had the effect of reducing the per cent of calcium sulfide in the product for all levels of carbon monoxide tested. For the range of 3 to 5 per cent carbon monoxide it was possible to reduce the amount of calcium

Figure 38. Effect of carbon dioxide on the per cent of calcium sulfide in the by-product

gas composition, 5% SO_2
temperature, 2140 to 2210°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh


40
30
20
10
0
0
5
10
15
20
25
30
35
5 % CO
4 % CO
3 % CO
CaS in by-product, %
CO_2 in feed gas, %

sulfide to insignificance by using a sufficiently high concentration of carbon dioxide. Of course, an increase in the level of carbon monoxide required a proportionate increase in the level of carbon dioxide to accomplish this.

Effect of sulfur dioxide The effect of sulfur dioxide concentration on the formation of calcium sulfide was studied at a nominal temperature of 2200°F and for single values of carbon dioxide concentration, mass velocity, and particle size. The results are plotted in Figure 39. No measurable amount of calcium sulfide was found in the by-product when no sulfur dioxide was fed. However, the addition of only 1 or 2 per cent sulfur dioxide to the feed produced noticeable amounts of calcium sulfide. On the other hand, further increases in the sulfur dioxide concentration failed to produce corresponding increases in the amount of calcium sulfide formed and in actuality there appeared to be some decrease in the amount as the level of sulfur dioxide was increased. Consequently the curves appeared to pass through maxima. But, of course, the actual shape of the curves is open to question since there was a wide scattering of points.

Comparison of anhydrite and gypsum In order to determine whether anhydrite would behave differently from gypsum several runs were made using -8 +9 mesh particles of anhydrite. Although this size was slightly smaller than the nearest size of gypsum particles (-7 +8 mesh), the difference was not thought to be great enough to make the comparison invalid. The comparison was made at several different levels of carbon monoxide and carbon dioxide while the other conditions were kept essentially constant. Sulfur dioxide was not included in any of the runs.

The observed maximum desulfurization rates are plotted in Figure 40

Figure 39. Effect of sulfur dioxide on the per cent of calcium sulfide in the by-product

gas composition, 10% CO_2
temperature, 2140 to 2220°F
mass velocity, 0.20 lb./sec. x sq.ft.
gypsum size, -7 +8 mesh

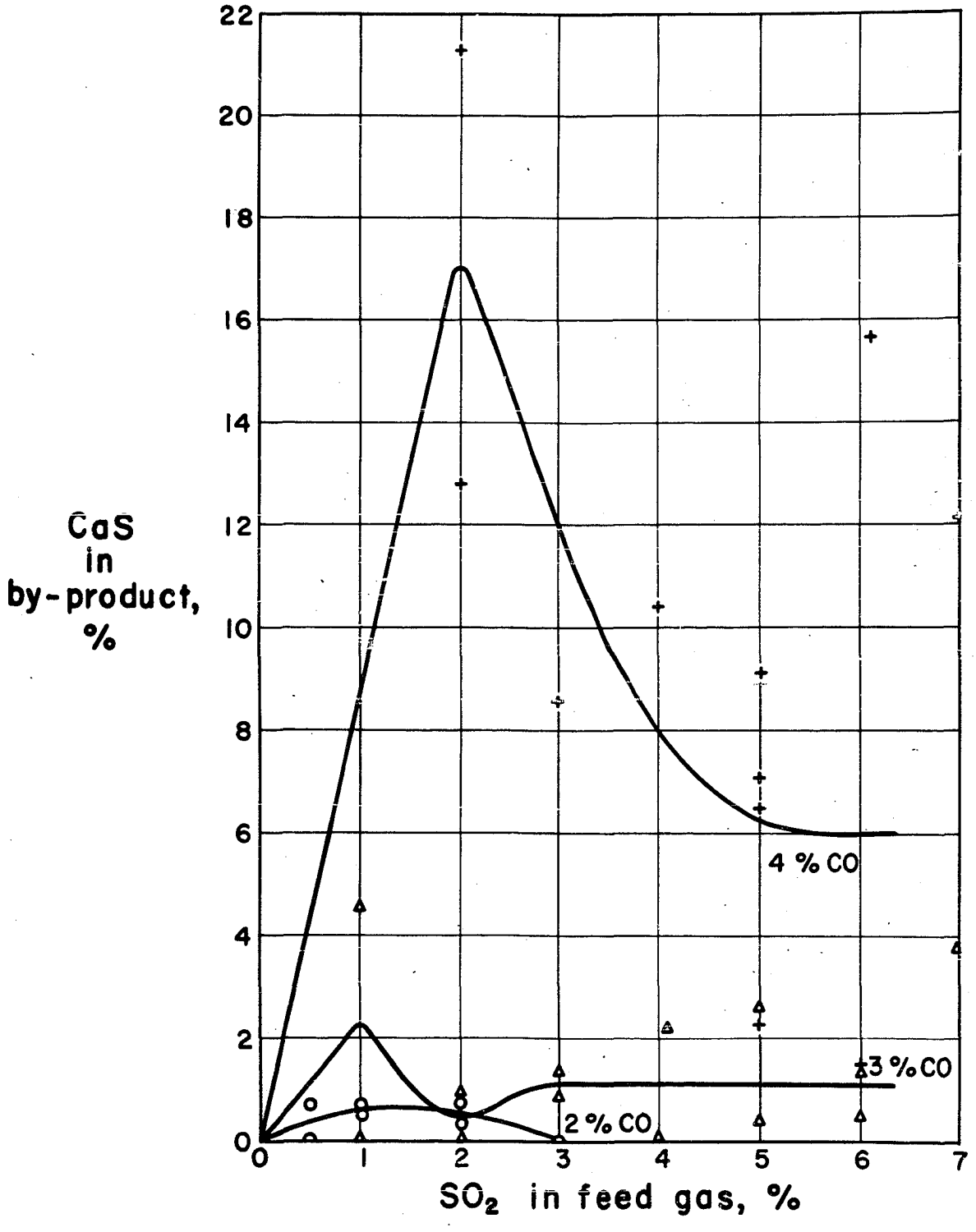
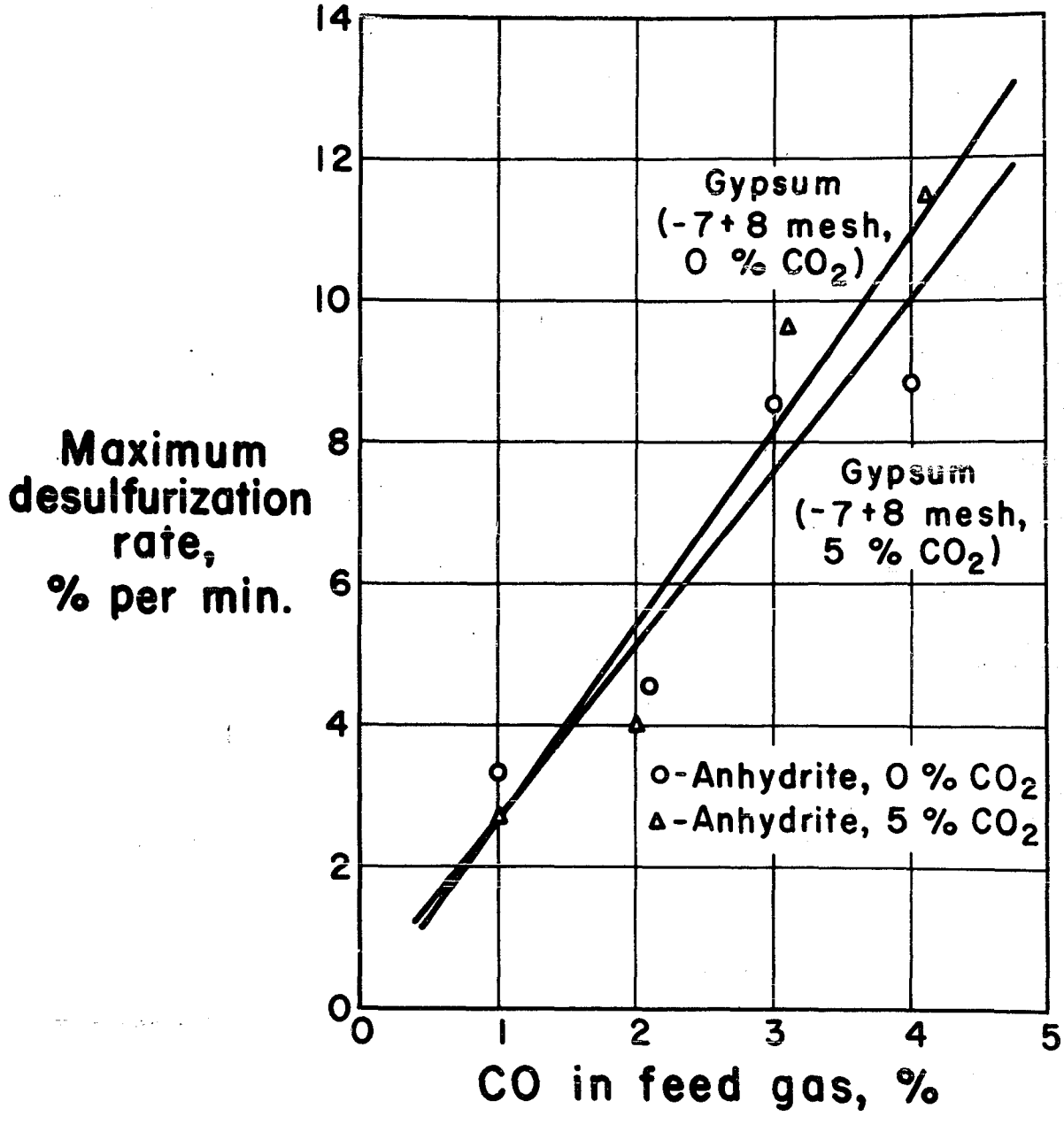

CaS in by-product, %
22
20
18
16
14
12
10
8
6
4
2
0
0
1
2
3
4
5
6
7
4 % CO
3 % CO
2 % CO
SO2 in feed gas, %

Figure 40. Comparison of the effect of carbon monoxide on gypsum and anhydrite respectively

gas composition, 0% SO_2
temperature, 2170 to 2240°F
mass velocity, 0.20 lb./sec. x sq.ft.
anhydrite size, -8 +9 mesh
bed depth, 1.0 in.


Maximum desulfurization rate, % per min.
14
12
10
8
6
4
2
0
0
1
2
3
4
5
CO in feed gas, %
Gypsum (-7+8 mesh, 0 % CO2)
Gypsum (-7+8 mesh, 5 % CO2)
o-Anhydrite, 0 % CO2
Δ-Anhydrite, 5 % CO2

as a function of the carbon monoxide concentration. For comparison the two lines shown are for -7 +8 mesh gypsum with 0 and 5 per cent carbon dioxide respectively. There is not a noticeable difference in the maximum desulfurization rates for gypsum and anhydrite.

The per cent of calcium sulfide found in the by-product is compared in Table 9. When the feed gas contained 2 or 4 per cent carbon monoxide and no carbon dioxide, it appeared that the anhydrite resulted in more calcium sulfide in the by-product. No difference was observed for other combinations of gas composition. However, a wide variation usually occurred in the per cent of calcium sulfide.

Table 9. Comparison of anhydrite and gypsum with respect to the per cent of calcium sulfide in the by-product

(0% SO_2, 2170 to 2250°F, mass vel. = 0.20 lb./sec. x ft.^{2})

Gas composition[a] mole %		CaS in product, %	
		Gypsum	Anhydrite
CO	CO_2	-7 +8 mesh	-8 +9 mesh
1	0	0.1 -	0
2	0	14.7, 17.0	24.4
4	0	27.2, 20.8	35.6
1	5	0 , 1.2	0
2	5	0 -	0
3	5	0 , 8.9	0
4	5	0 -	0.9

[a]Remainder nitrogen.

Comparison of water vapor and carbon dioxide A comparison was made of the relative effects produced by water vapor and carbon dioxide on the desulfurization rate and amount of calcium sulfide in the by-product for several sets of conditions where carbon monoxide was the reducing gas. The results are given in Table 10. No noticeable difference in the maximum desulfurization rate was observed between the runs made with water vapor and those made with carbon dioxide. When there was no sulfur dioxide present in the feed gas, water vapor appeared to be as effective as carbon dioxide in preventing the formation of calcium sulfide. Although there appeared to be some difference in the amount of calcium sulfide at the 5 per cent level of sulfur dioxide, the evidence was inconclusive because the variation in results was relatively large.

Since water vapor and carbon dioxide seemed to be about equally effective in reducing calcium sulfide formation, a surface adsorption phenomenon might be involved. Perhaps the adsorption of these gases on the surface of the solids interrupted the sulfide producing reaction.

Comparison of hydrogen and carbon monoxide A comparison was made of the relative effects produced by hydrogen and carbon monoxide in the desulfurization rate and amount of calcium sulfide in the by-product for several sets of conditions. The results are given in Table 11. For each set of conditions the maximum desulfurization rate was substantially larger when hydrogen was used as the reducing gas in place of carbon monoxide. With respect to the amount of calcium sulfide any difference produced by the type of reducing gas appeared to be slight.

Table 10. Comparison of the relative effects of water vapor and carbon dioxide

(-7 +8 mesh gypsum)

Run no.	Mass vel. lb./sec. x ft.^{2}	Gas composition[a] mole %	Temp.[b] °F	CaS %	Max. rate %/min.
32	0.314	1.0 CO, 3.4 H_2O,	2200	0	3.85
85	0.299	1.0 CO, 5.3 CO_2	2200	0	3.80
45	0.102	2.0 CO, 3.9 H_2O	2230	0.04	4.59
80	0.101	2.0 CO, 5.9 CO_2	2210	0	3.44
93	0.100	2.0 CO, 5.0 CO_2	2210	0	2.82
58	0.200	1.9 CO, 5.2 H_2O	2210	0	4.59
62	0.200	2.0 CO 5.0 CO_2	2220	0	4.56
208	0.204	3.9 CO, 12.2 H_2O, 4.9 SO_2	2180	2.24	15.93
209	0.203	3.9 CO, 11.6 H_2O, 4.9 SO_2	2190	5.47	12.16
101	0.200	4.0 CO, 9.9 CO_2, 5.0 SO_2	2180	7.11	12.20
143	0.200	4.0 CO, 9.9 CO_2, 5.0 SO_2	2210	2.27	14.75
158	0.200	4.0 CO, 9.9 CO_2, 5.0 SO_2	2180	9.11	13.16

[a]Remainder nitrogen.

[b]Mean outlet temp. during max. desulfurization rate period.

Discussion of Results

The results of this investigation show that gypsum can be almost completely desulfurized at relatively rapid rates under the proper conditions. In a neutral atmosphere gypsum will decompose at an appreciable rate but it will not decompose in an atmosphere containing more than a trace of its gaseous decomposition products below its sintering temperature. The equilibrium seems to be limiting rather than the decomposition rate, but in

Table 11. Comparison of the relative effects of hydrogen and carbon monoxide

(-7 +8 mesh gypsum)

Run no.	Mass vel. lb./sec. x ft.^{2}	Gas composition[a] mole %	Temp.[b] °F	CaS %	Max. rate %/min.
20	0.116	2.0 H_2	2250	13.85	6.54
47	0.099	2.1 CO	2250	6.44	3.75
57	0.099	2.0 CO	2220	12.47	3.26
30	0.286	1.0 H_2, 4 H_2O	2160	0	8.93
32	0.314	1.0 CO, 3.4 H_2O	2200	0	3.85
85	0.299	1.0 CO, 5.3 CO_2	2200	0	3.80
128	0.197	4.1 H_2, 8.5 H_2O, 5.1 SO_2	2080	36.6	21.3
129	0.196	4.0 H_2, 12.9 H_2O, 5.1 SO_2	2100	32.9	25.6
155	0.200	4.0 CO, 9.9 CO_2, 5.0 SO_2	2100	31.0	8.06
161	0.200	4.0 CO, 9.9 CO_2, 5.0 SO_2	2100	40.8	6.34

[a]Remainder nitrogen.

[b]Mean outlet temp. during max. desulfurization rate period.

any event thermal decomposition does not seem to offer a practical method for desulfurizing gypsum.

The fact that gypsum will decompose rapidly and almost completely in the presence of a gas phase containing 2 to 5 per cent carbon monoxide, 20 per cent carbon dioxide, and 5 per cent sulfur dioxide tends to show that reductive decomposition is a feasible method. Moreover the results of this study indicate approximate ranges of conditions which must be provided for such a process. Thus 2200 to 2250°F seems to be the optimum temperature range. At a lower temperature an excessive amount of calcium

sulfide may be produced, while at a higher temperature the desulfurization rate falls off and the solids start to sinter. The mass velocity of the gas should be as high as possible and the particle size as small as practical in order to provide the highest possible desulfurization rate. To minimize the amount of calcium sulfide produced, the composition of the gas phase must be very carefully controlled. It appears that carbon monoxide must be limited to concentrations of about 5 per cent or less. Carbon dioxide or water vapor tends to prevent or limit calcium sulfide in the by-product lime. The concentrations of these gases must be in proportion to the concentrations of carbon monoxide and sulfur dioxide.

For a limited range of conditions anhydrite gives about the same results as gypsum. When hydrogen is used in place of carbon monoxide, much faster desulfurization rates result but the per cent of calcium sulfide is not noticeably different.

In carrying out the experimental work relatively thin beds of gypsum were used so as to minimize the temperature and gas concentration gradients across the bed. The question remains unanswered as to what might take place in a thick bed such as might be encountered in a commercial reactor. One possibility is that the concentration of some gaseous product such as free sulfur might build up to the point where it would affect the kinetics.

In correlating the results, the composition of the gas fed to the reactor was used. The mean composition of the gas in the reactor should have been used but this was not known. However, this error was probably no greater than the error made in estimating the temperature.

Within the limits of this investigation it was possible to make rough

estimates concerning the rate controlling mechanism. The data indicate that the same mechanism was not controlling throughout the range of experimental conditions. When sulfur dioxide was fed, the "S" shaped desulfurization curves which resulted were a rather good indication that the same mechanism did not control throughout an individual run. Further evidence that the mechanism changed during a run was that the initial and maximum desulfurization rates were not affected in the same way by temperature, mass velocity, particle size, and gas composition. In comparing the maximum desulfurization rates observed for different conditions there was some evidence that when the feed gas contained 3 per cent carbon monoxide, 20 per cent carbon dioxide, and 5 per cent sulfur dioxide diffusion through the pores in the solid was controlling. When the carbon dioxide and sulfur dioxide were eliminated, the mass transfer rate across the outside gas film seemed more likely to be limiting.

INVESTIGATION OF A SHAFT FURNACE PROCESS

The thermal decomposition of gypsum in a shaft furnace under oxidizing conditions was investigated by Bollen (12) both below and above the fusion point. The process appeared unworkable and the investigation was shifted to a fluidized bed process. As a result of the fluidized bed study the discovery was made that reducing conditions favored the decomposition. Since a shaft furnace is a much simpler piece of equipment than a fluidized bed reactor, Bollen recommended that operation of a shaft furnace with reducing conditions be considered.

As a consequence an investigation was undertaken to demonstrate on a pilot plant scale the shaft furnace process with reducing conditions. The specific objectives of this investigation were to determine

1. the suitability of a shaft furnace for desulfurizing gypsum
2. the concentration of sulfur compounds in the off-gas
3. the quality of by-product lime produced.

Process Description

The process involved heating and reacting a descending column of crushed and sized gypsum in a refractory lined shaft furnace with an ascending stream of hot reducing gases produced by burning natural gas with a limited air supply. The natural gas was burned either directly in the bed of solids or in an external combustion chamber. In the former case, a mixture of natural gas and primary air was introduced part way up the shaft while secondary air was introduced near the bottom so that it served to cool the solids and recover some of the heat. In the case of

external combustion, the hot gases were introduced part way up the shaft and below this point the solids were cooled only by conduction of heat through the walls. The ratio of air to natural gas was controlled to provide a reducing gas of the proper composition. Ideally the off-gas could be used for the production of sulfuric acid while the solid product would be a relatively pure lime requiring no further processing.

According to the American Gas Association Committee on Industrial Gas Research (1) natural gas burned with insufficient air for complete combustion should yield a reducing gas containing about equal concentrations of carbon monoxide and hydrogen, the combined concentration of these components being inversely proportional to the percentage of the air required for complete combustion.

The pilot plant was designed for semicontinuous operation; gypsum was added intermittently and solids were withdrawn intermittently. As the gypsum passed down the shaft it successively underwent dehydration, heating, reaction with reducing gases, and cooling.

Raw Material

Gypsum used in the shaft furnace operation came from the United States Gypsum Company mine at Fort Dodge, Iowa. It was crushed in a small jaw crusher and then separated into relatively narrow size fractions. The size separation was carried out by means of a shaking screen having two decks of square mesh, woven wire screens each 12 inches wide by 36 inches long. Two size fractions, $-\frac{1}{2}$ + 3/8 inch and -3/4 $+\frac{1}{2}$ inch, were employed. Chemical and sieve analyses of these fractions appear in Table 12. The

Table 12. Chemical and screen analyses of gypsum

Constituent	Per cent of sample, dry basis -3/4 +½ in.	-½ +3/8 in.
H_2O (combined)	17.4	17.8
CaO	31.6	30.9
MgO	0.2	0.1
SO_3	45.5	45.7
CO_2	0.7	0.7
R_2O_3	0.2	0
SiO_2	1.9	2.9
NaCl	0.3	0.3
Total	97.8	98.4
Screen opening, in.		
-0.742 + 0.525	65.6	0
-0.525 + 0.371	32.3	71.4
-0.371 + 0.263	1.1	26.6
-0.263	0.7	-
-0.263 + 0.185	-	1.0
-0.185	-	0.9
Total	99.7	99.9

American Society for Testing Materials standard method, designation C 26-52 (2), was used for the chemical analyses.

Description of Equipment

For demonstrating the process a pilot plant scale shaft furnace was built of K-28 insulating firebrick set with refractory cement and supported by a steel framework. The 6½ inch diameter by 5 foot tall shaft was formed by ramming chrome plastic (manufactured by the Laclede-Christy Company) around a cylindrical form placed inside the brickwork. The construction is shown in Figure 41, which is a photograph of the partially completed furnace. During the design stage it was assumed that the refractory walls would be gas tight. However, upon heating, numerous large cracks developed in the lining and a few extended clear through the walls. Therefore, it was necessary to completely encase the furnace with welded steel plate to make it gas tight. Figure 42 is a photograph of the completed furnace. Some of the furnace details are shown in Figure 43.

The top of the furnace was enclosed by a flanged steel cover lined with Plicast No. 31 castable refractory manufactured by the Plibrico Company. It had connections for the off-gas piping, feed hopper, centerline thermowell, and one of the gas sampling pipes. Except when gypsum was being introduced, the hopper outlet was closed with a rubber stopper.

The centerline thermowell was designed to extend down through the hottest portion of the bed. Finding a suitable material for the thermocouple well was a problem. Thermowells made of ¼ inch pipe of either type 304 or 446 stainless steel failed after a few days or sometimes even

Figure 41. Shaft furnace under construction

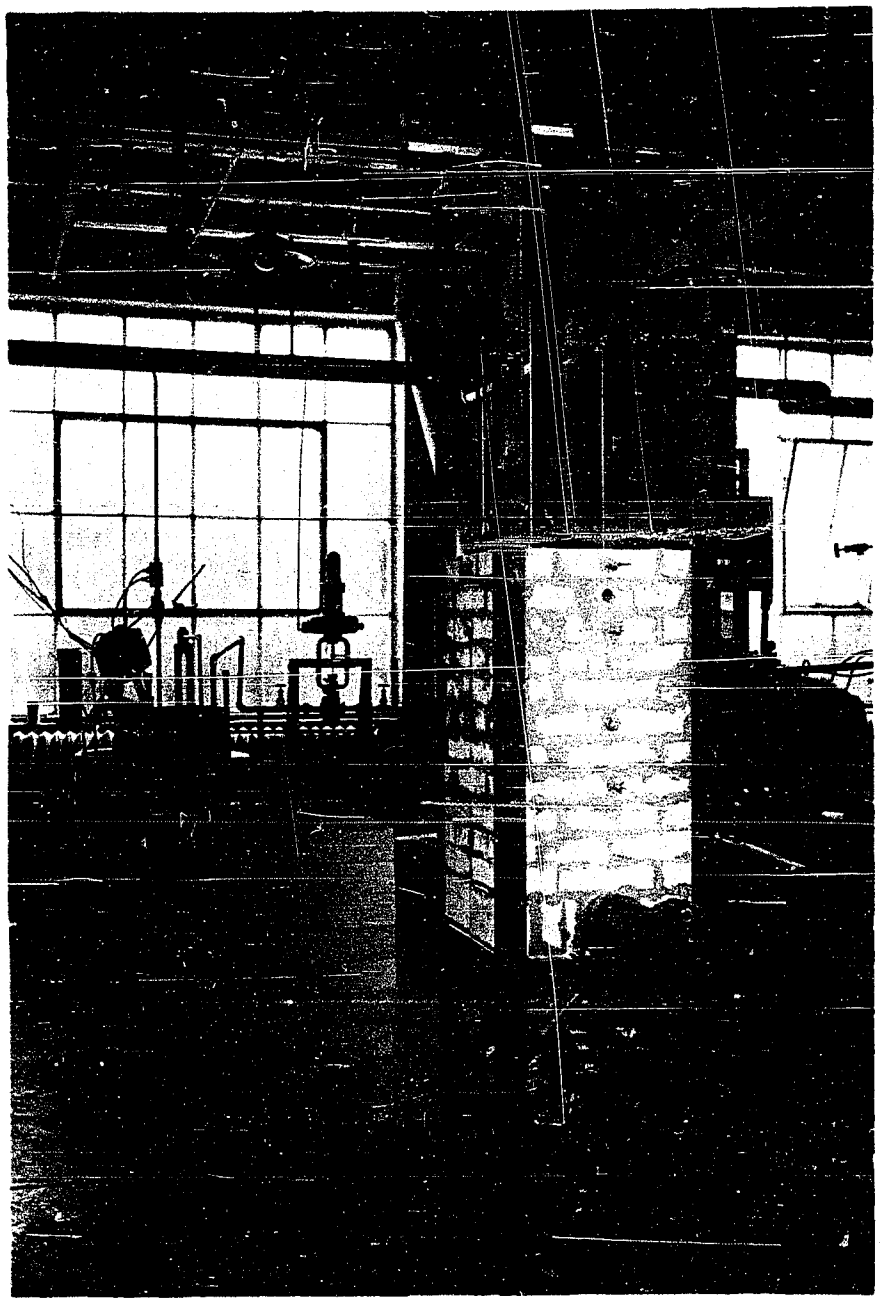


Figure 42. Completed shaft furnace

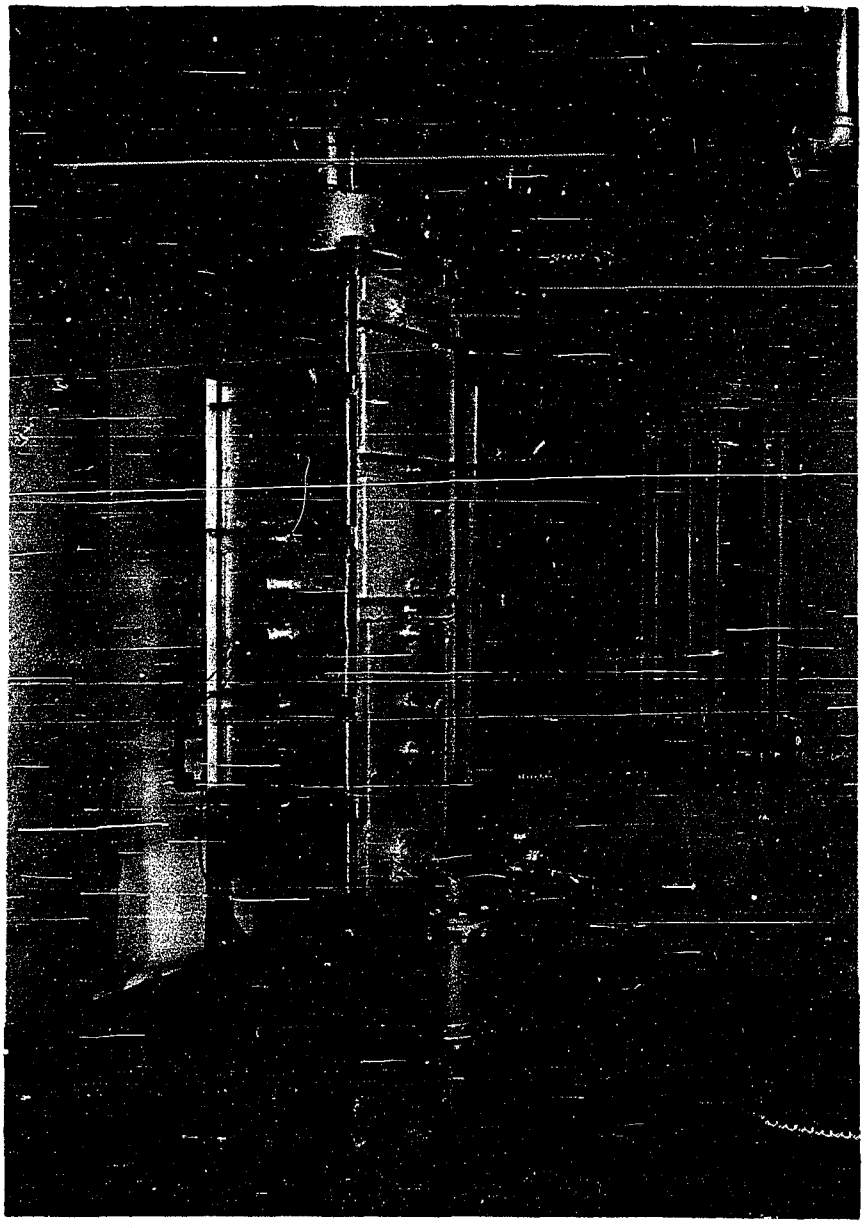
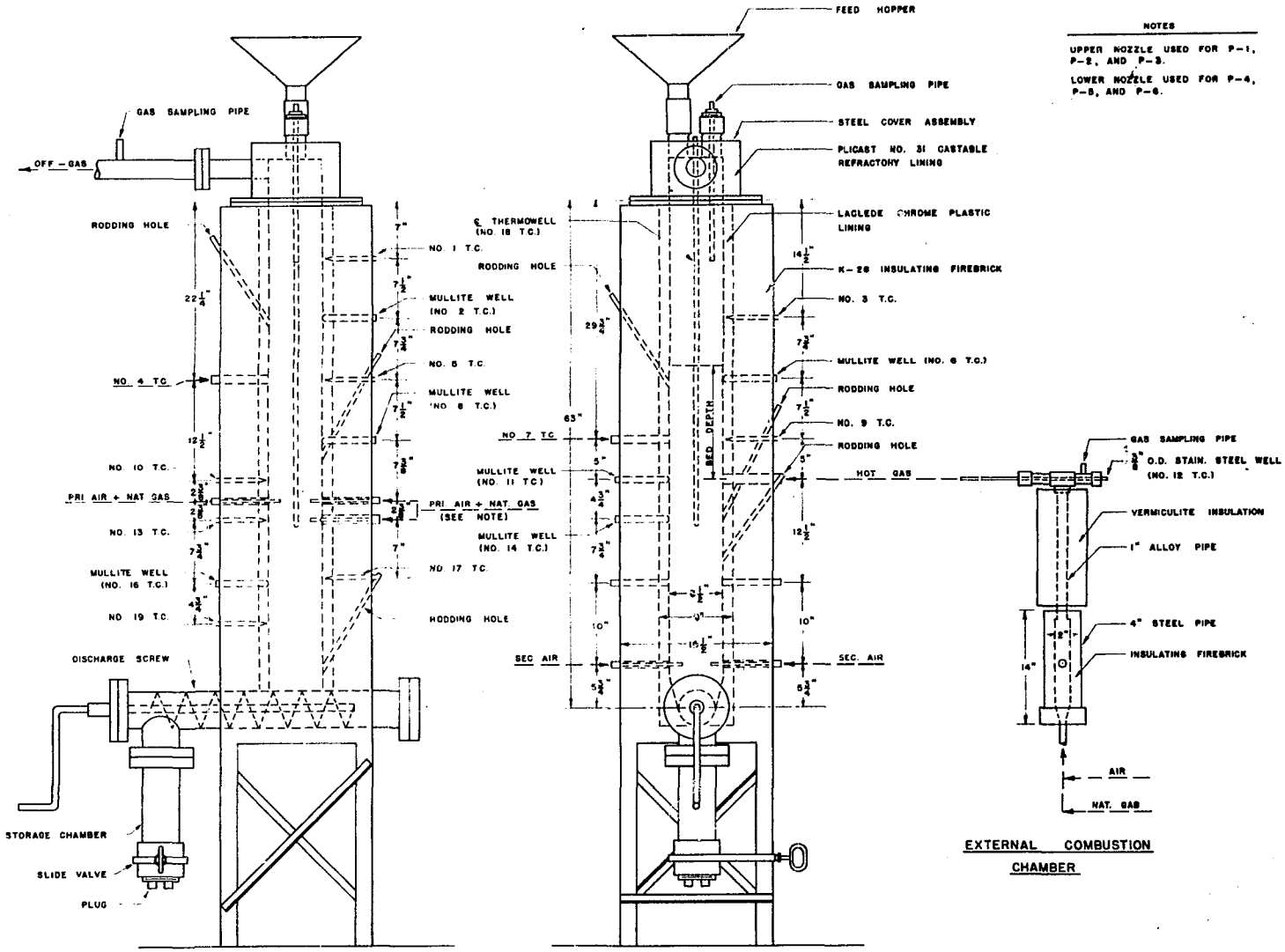


Figure 43. Details of shaft furnace


GAS SAMPLING PIPE
OFF-GAS
RODDING HOLE
NO. 1 T.C.
MULLITE WELL (NO. 2 T.C.)
RODDING HOLE
NO. 5 T.C.
NO. 4 T.C.
MULLITE WELL (NO. 8 T.C.)
NO. 10 T.C.
PRI AIR + NAT GAS
NO. 13 T.C.
MULLITE WELL (NO. 16 T.C.)
NO. 19 T.C.
DISCHARGE SCREW
STORAGE CHAMBER
SLIDE VALVE
PLUG
WEST ELEVATION
FEED HOPPER
GAS SAMPLING PIPE
STEEL COVER ASSEMBLY
PLICAST NO. 31 CASTABLE REFRACTORY LINING
℄ THERMOWELL (NO. 18 T.C.)
LACLEDE CHROME PLASTIC LINING
RODDING HOLE
K-26 INSULATING FIREBRICK
NO. 3 T.C.
MULLITE WELL (NO. 6 T.C.)
RODDING HOLE
NO. 7 T.C.
NO. 9 T.C.
RODDING HOLE
MULLITE WELL (NO. 11 T.C.)
PRI AIR + NAT. GAS (SEE NOTE)
MULLITE WELL (NO. 14 T.C.)
NO. 17 T.C.
RODDING HOLE
BED DEPTH
SEC AIR
SEC. AIR
HOT GAS
NORTH ELEVATION
NOTES
UPPER NOZZLE USED FOR P-1, P-2, AND P-3.
LOWER NOZZLE USED FOR P-4, P-5, AND P-6.
GAS SAMPLING PIPE
O.D. STAIN. STEEL WELL (NO. 12 T.C.)
VERMICULITE INSULATION
1" ALLOY PIPE
4" STEEL PIPE
INSULATING FIREBRICK
AIR
NAT. GAS
EXTERNAL COMBUSTION CHAMBER

a few hours. Of these two stainless steels, type 446 seemed to have the better corrosion resistance. A metal-ceramic LT-1 protecting tube manufactured by the Bristol Company with an outside diameter of 7/8 inch and a wall thickness of 1/8 inch was eventually found to stand up under the conditions of operation.

Several openings were provided in the walls for admitting gases, for rodding the bed of solids, and for admitting thermocouples. Steel pipe nipples were cemented into the openings and welded to the steel shell. Through four of the nipples $\frac{1}{4}$ inch steel pipe nozzles were inserted about $1\frac{1}{2}$ inches into the shaft. Natural gas mixed with primary air was fed through two nozzles, located on opposite sides of the furnace and about two-fifths of the way up the shaft. Secondary air was introduced through the other two nozzles, located on opposite sides near the bottom of the shaft. The upper steel nozzles were exposed to the highest kiln temperatures and burned out rapidly. They were replaced with nozzles made of type 446 stainless steel which provided limited service. Through other of the nipples chromel-alumel thermocouples in protection tubes were inserted for measuring bed temperatures. For exposures of a few hours tubes made of type 304 stainless steel were satisfactory, but for longer periods of service mullite tubes were used.

Since it was considered desirable to have a minimum number of obstructions to the flow of solids in the shaft, provision was made for measuring lining temperatures with the hope that these temperatures could be used for controlling the operation and would eliminate the need for inserting temperature sensing elements into the descending bed. Bare chromel-alumel thermocouples of heavy gauge wire (A.W.G. no. 11) and

mullite thermocouple protection tubes were inserted through the walls and embedded in the lining. The ends of the mullite tubes were flush with the inner surface of the lining but the ends of the bare thermocouples were located about $\frac{1}{4}$ inch from the surface. Chromel-alumel thermocouples (A.W.G. no. 20) were installed in the mullite tubes.

For discharging the solids from the bottom of the furnace a hand operated screw conveyor was provided. Two screws were used interchangeably. One was made of cast iron and had a diameter of 3-21/32 inches and a constant pitch of $3\frac{1}{2}$ inches. The other was made of welded steel and had a diameter of 3-21/32 inches and a pitch varying from 3-5/8 to 4-7/8 inches. Both were housed in a 4 inch steel pipe. Solids discharged by the screw conveyor fell into a short section of 4 inch pipe which served as a storage chamber. The latter could be emptied periodically by opening a slide valve. Since this valve did not provide a good seal, its outlet was kept plugged.

Two natural gas lines, two primary air lines, and two secondary air lines were required for the operation. Each line was equipped with an orifice plate so that the flow rate could be determined. Water filled manometers were used for measuring the pressure drops across the orifice plates. These flow meters were calibrated with a diaphragm type, positive displacement gas meter.

An ejector operated by compressed air was used for producing a furnace draft. The gases from the furnace were conducted by the off-gas piping to the ejector and discharged to the atmosphere.

After it was found that the composition of the gas in the kiln could not be controlled within the desired limits, an external combustion chamber

was added. It was constructed from a short section of 4 inch steel pipe and lined with K-28 insulating firebrick. The combustion space was about 2 inches in diameter and 10 inches long. Premixed air and natural gas were introduced through a 3/8 inch steel pipe at the lower end. The gas velocity was sufficiently high to prevent flash back. The hot gas was conducted through a 1 inch partially insulated alloy pipe to the furnace. A tee inserted in the line provided a means for introducing a 3/8 inch diameter stainless steel thermowell and a connection for gas sampling. With the addition of the external combustion chamber, the nozzles which had formerly been used for introducing natural gas and air were removed. At first no means was provided for distributing the hot gas uniformly across the bed. It entered at one point at the side of the bed with the result that the gas flow and temperature were greater along that side. To provide better distribution of the hot gas, a distributor was installed before the P-12 series of runs. It was made of $\frac{1}{2}$ inch pipe of type 347 stainless steel and contained a number of small holes through which the gas entered the bed. It completely disintegrated during the operation which followed.

The original design of the piping between the combustion chamber and the furnace, coupled with the low natural gas supply pressure, proved to be a serious limitation. The pressure drop restricted the rate of flow of hot gas and the material of construction limited the maximum gas temperature. Since only a part of the line could be insulated without having it burn out, the gas was usually cooled more than was desirable before it reached the bed of solids.

Subsequently, a new natural gas supply was installed and the gas

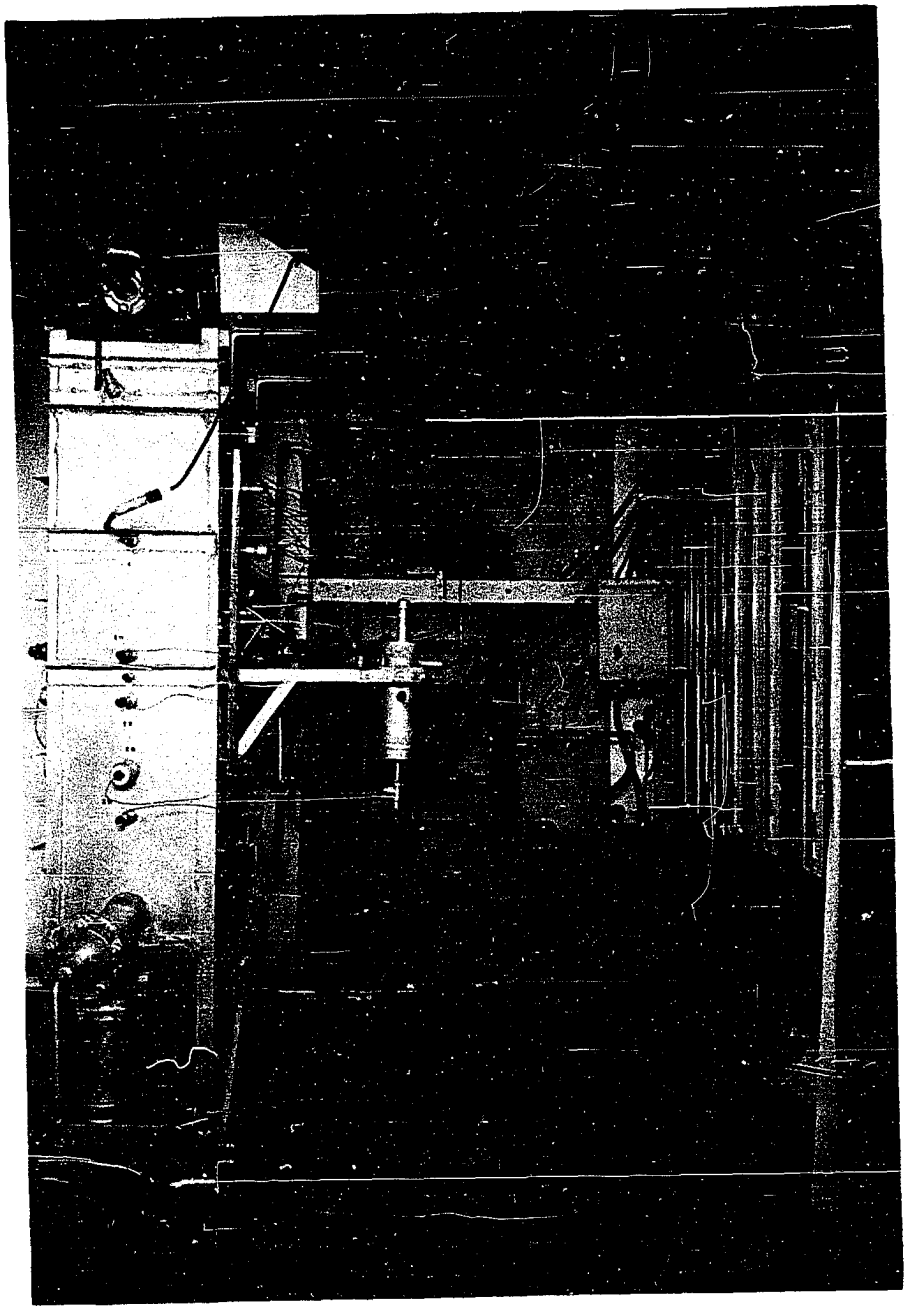
pressure raised. The hot gas piping was revamped and a Bristol metal-ceramic LT-1 thermocouple protecting tube was adapted for carrying the hot gas. The closed end of the tube was cut off at an angle and this end was allowed to project 2-3/4 inches into the bed of solids. Since some cooling of the hot gas was needed, a 11½ inch long portion of the tube was left exposed to the atmosphere. To provide further cooling when needed compressed air could be directed against the tube from a number of small orifices located in an air line just above the tube. The modified hot gas line and cooling arrangement is shown in Figure 44. The combustion chamber is located in the center of the photograph and the metal-ceramic tube runs almost horizontally between the upper end of the combustion chamber and the furnace. The connection on the upper right-hand side of the chamber was used for sampling the combustion products. These changes were incorporated before making the final run (P-13).

Temperature Distribution

In this work no attempt was made to measure the distribution of gas velocities and phase compositions throughout the furnace. Only the amount and composition of the materials entering and leaving were determined. However, in order to have some indication of the nonhomogeneous character of the system, temperature profiles were determined both along and at right angles to the major axis of the shaft. These were found by moving thermocouples in and out of their respective protection tubes which were installed in the bed.

Typical longitudinal temperature profiles obtained with Thermocouple

Figure 44. Combustion chamber and modified hot gas piping



18 are shown in Figure 45 while transverse profiles determined with Thermocouples 4 and 7 are shown in Figures 46 and 47 respectively. These temperature measurements were made after the incorporation of the outside combustion chamber. Operating conditions which may have had some influence on the shape of the profiles are given in Table 13. Most of the profiles represent periods when the bed was static and when little or no reaction was taking place. Thus during Run P-7 and shortly before the start of Run P-12-A any reaction which may have occurred must have been very slow due to the presence of neutral or oxidizing atmospheres and of solids charged which were the product of previous runs and already partly decomposed. Only Profiles VII and X represent periods when the reaction rate should have been perceptible.

It is likely that the gas flow through the bed was in the turbulent region. This inference arises from a logarithmic plot of bed pressure drop against total gas rate in Figure 48 for data taken during Run P-7. The plotted points lie very close to a straight line having a slope of 1.85 which according to Perry (44, p. 393) would be indicative of turbulent flow. In the other operating periods for which profiles are given, the total gas flow rates were of the same order of magnitude and the average particle size was probably larger, so that turbulent flow should have prevailed.

Temperature Profiles I, II and III were obtained when the operating conditions were substantially the same and are representative of the temperature distribution when the bed was fixed and the reaction rate was small or negligible. Profile I portrays the temperature measured along the vertical centerline and it shows that the bed temperature reached a

Figure 45. Longitudinal temperature profiles obtained with Thermocouple 18

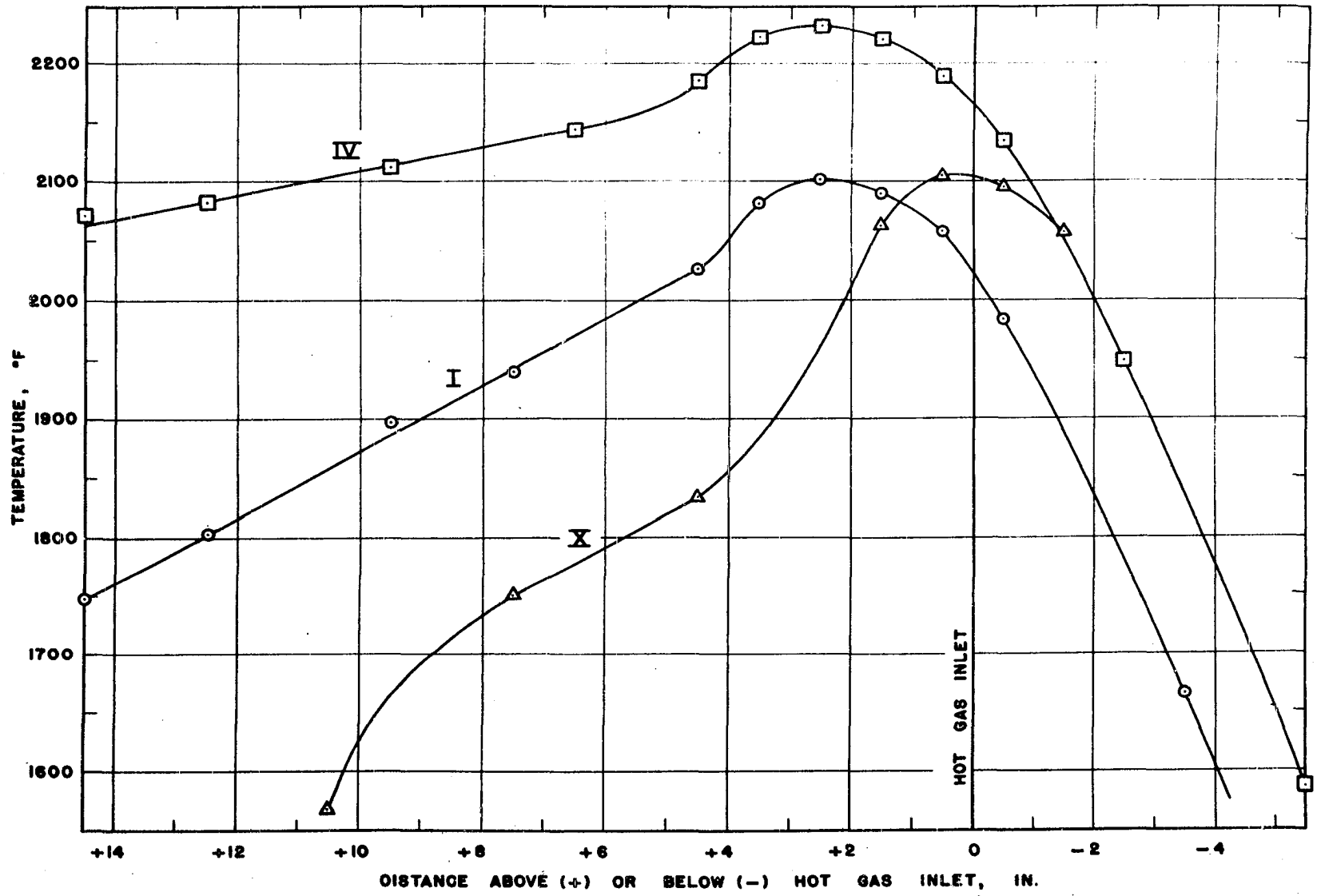

2200
2100
2000
1900
1800
1700
1600
TEMPERATURE, °F
IV
I
X
HOT GAS INLET
+14
+12
+10
+8
+6
+4
+2
0
−2
−4
DISTANCE ABOVE (+) OR BELOW (−) HOT GAS INLET, IN.

Figure 46. Transverse temperature profiles obtained with Thermocouple 4

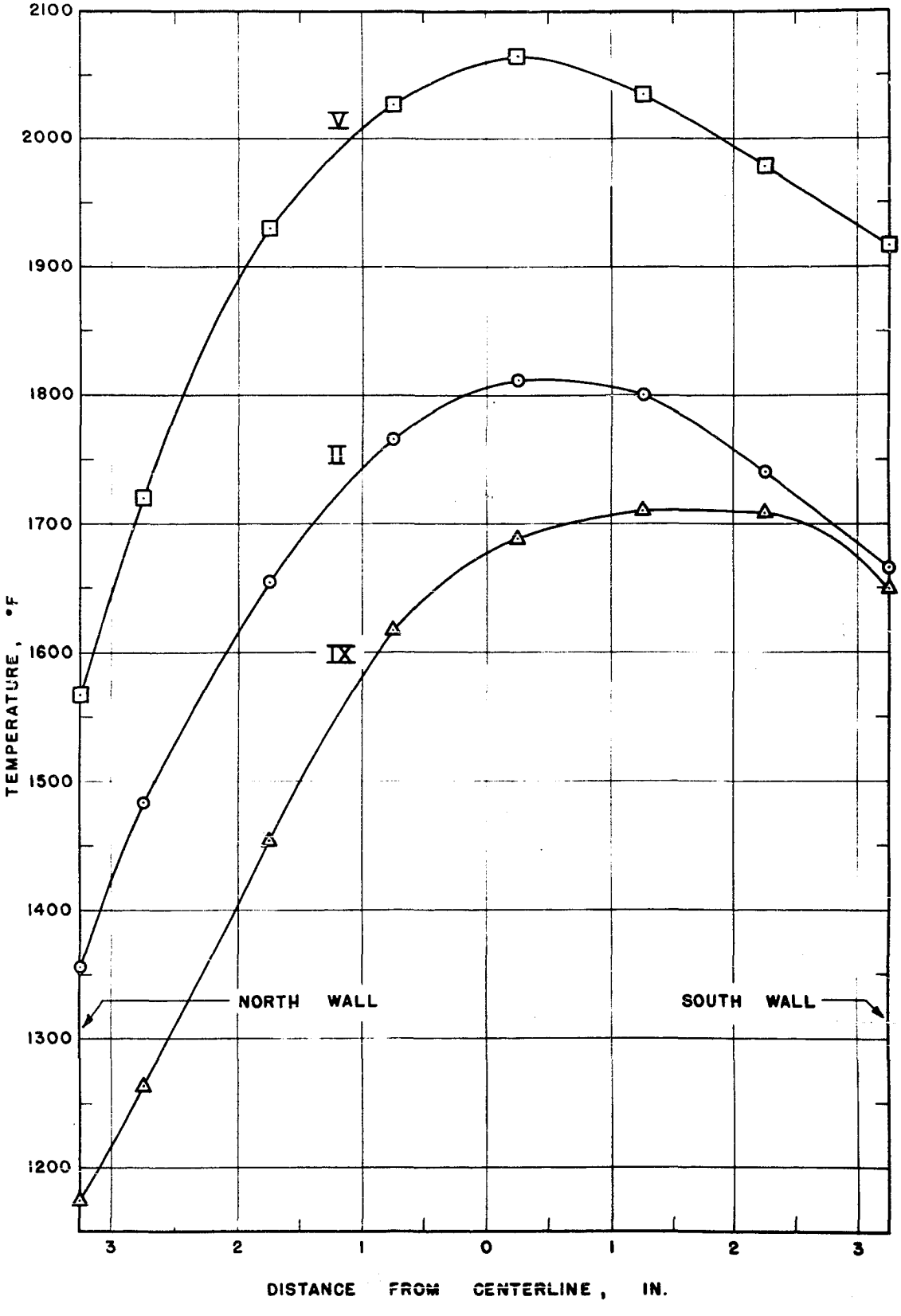

2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
TEMPERATURE, °F
V
II
IX
NORTH WALL
SOUTH WALL
3
2
1
0
1
2
3
DISTANCE FROM CENTERLINE, IN.

Figure 47. Transverse temperature profiles obtained with Thermocouple 7

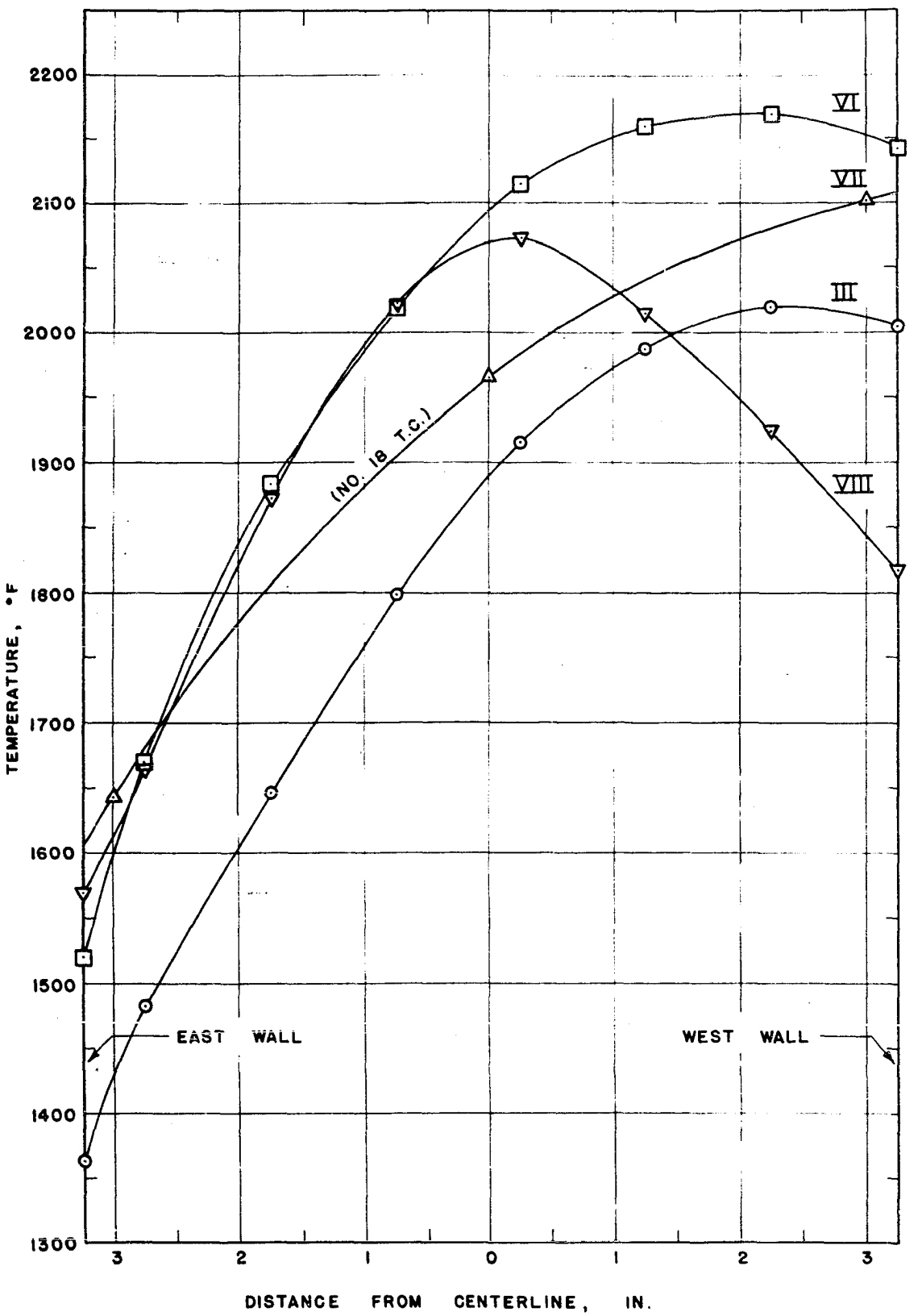
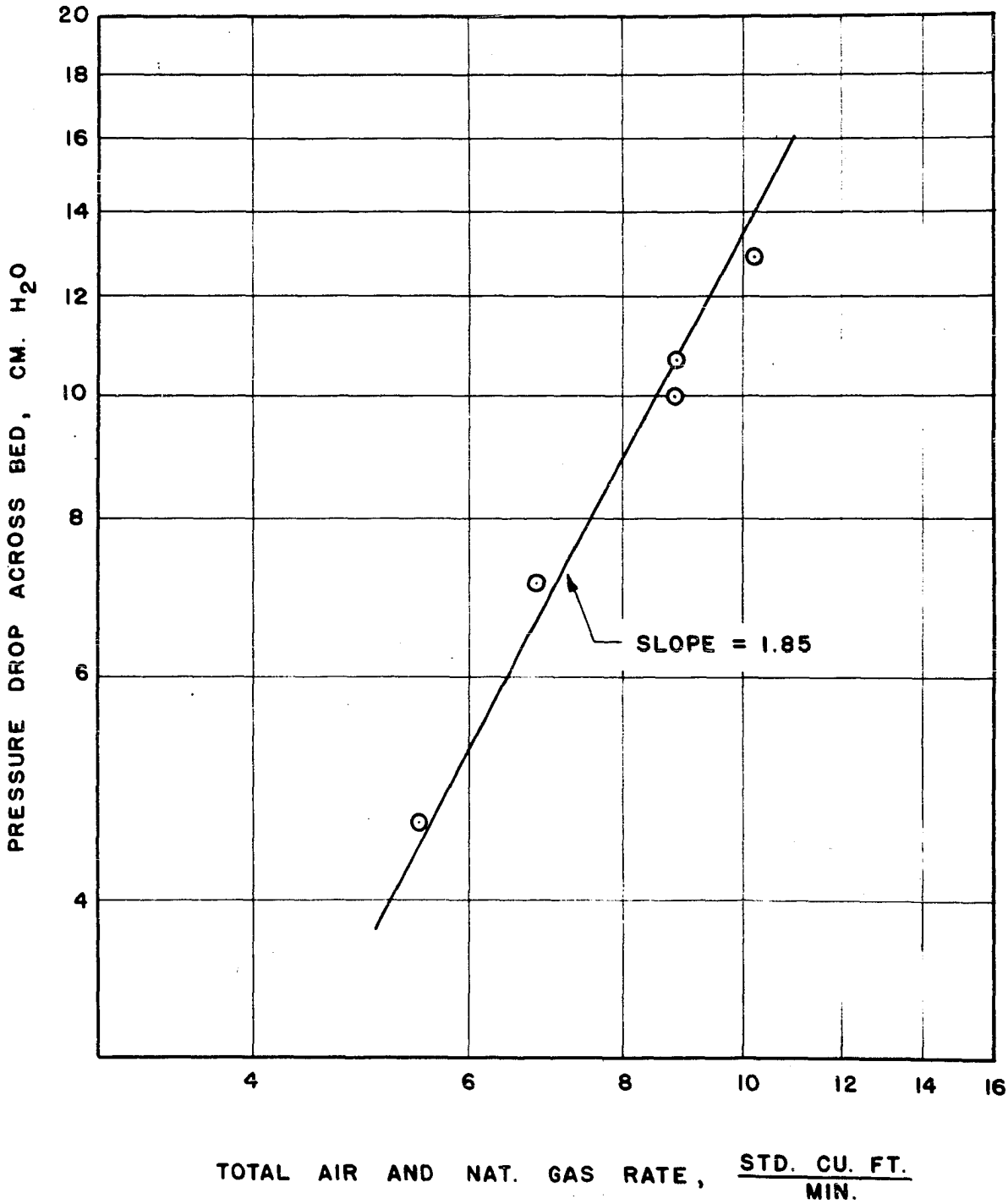

2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
TEMPERATURE, °F
VI
VII
III
VIII
(NO. 18 T.C.)
EAST WALL
WEST WALL
3
2
1
0
1
2
3
DISTANCE FROM CENTERLINE, IN.

Table I3. Operating conditions corresponding to temperature profiles

Profile no.	Run no.	Date	Time	Air rate s.c.f.m.	Natural gas rate s.c.f.m.	Solids discharge rate lb./hr.	Bed depth in.	Type of atmosphere
I	P-7	2-25-56	2045	6.3	0.62	0	29-35	Neutral
II	P-7	2-25-56	2235	6.2	0.63	0	29-35	Neutral
III	P-7	2-25-56	2250	6.2	0.64	0	29-35	Neutral
IV	P-7	2-26-56	1140	9.3	0.86	0	29-35	2% O_2
V	P-7	2-26-56	1145	9.3	0.86	0	29-35	2% O_2
VI	P-7	2-26-56	1150	9.3	0.86	0	29-35	2% O_2
VII	P-11-B	4-16-56	2230	5.8	0.60	2	17	1% CO
VIII	P-12-A[a]	5-18-56	2035	6.1	0.59	0	15	Neutral
IX	P-12-A[a]	5-18-56	2125	6.1	0.59	0	17	Neutral
X	P-12-B	5-20-56	1725	5.5	0.55	2	12	1% CO

[a]Represents conditions shortly before the start of Run P-12-A.

Figure 48. Bed pressure drop for various gas flow rates, Run P-7


PRESSURE DROP ACROSS BED, CM. H_2O
20
18
16
14
12
10
8
6
4
SLOPE = 1.85
4
6
8
10
12
14
16
TOTAL AIR AND NAT. GAS RATE, STD. CU. FT. / MIN.

maximum 2.5 inches above the centerline of the hot gas inlet which was located at one side of the bed. The temperature decreased on either side of the maximum because of heat losses through the furnace walls. Profile III represents the temperature observed along a horizontal line 5 inches directly above and parallel to the hot gas inlet. It indicates that the bed was much hotter on the side in which the hot gas inlet was located. Profile II depicts the temperature along a horizontal line 12.5 inches above and running at right angles to the hot gas inlet centerline. It shows that the center of the bed was appreciably hotter than the sides. The side next to the north wall was probably cooler than the opposite side because the thermocouple and its protection tube were introduced through the north wall.

To show the effect of a 50 per cent higher total gas flow rate on the temperature distribution, Profiles IV, V and VI are given. The principal effect of the higher gas rate was an increase in bed temperature, probably due to the proportionately smaller heat loss, especially in the piping between the combustion chamber and the shaft of the furnace. The proportionately smaller heat loss through the walls caused the longitudinal profile to drop less rapidly but seemed to have little effect on the shape of the transverse profiles.

In seeking to obtain a more uniform temperature distribution a hot gas distributor was installed prior to Run P-12-A and Profile VIII (Figure 47) and Profile IX (Figure 46) resulted. A comparison of Profile VIII with III (Figure 47) indicates a shift in the peak temperature from one side to the center of the bed, probably caused by a corresponding shift in the gas flow.

To illustrate the situation where the bed was descending intermittently

and some reaction was taking place, Profile VII (Figure 47) and X (Figure 45) are presented. Profile X is obviously more peaked than the other longitudinal profiles and this may have been the result of the endothermic reaction. Since the bed depth above the hot gas inlet was only 12 inches, it is not surprising that there is a break in the curve at about the 10 inch level, for considerable heat would have been absorbed in the top layer of particles to dehydrate the gypsum. Profile VII is a transverse profile made along the horizontal centerline of the hot gas inlet by inserting a protected thermocouple (T.C. 18) into the bed from above. This could be done because the furnace cover was removed for the run. The profile has the same general shape as those made on a parallel line 5 inches above but with a thermocouple inserted from the side.

The temperature profiles indicate that the bed temperature was far from uniform even though the gas flow was in the turbulent region. For the case where the bed was stationary and little reaction was taking place the causes of this nonuniformity seemed to be the relatively great heat loss through the furnace walls and the poor distribution of the entering hot gas. Where the bed was moving intermittently and some reaction was occurring the temperature gradients were further increased because of the heat absorbed by the solids, which included sensible heat, heat of dehydration, and heat of reaction.

The large temperature gradients throughout the bed coupled with the appreciable thermal conductivity of the thermocouples and protection tubes caused some error in temperature measurements. Some indication of the magnitude of the error is given by comparing the temperatures indicated simultaneously by a thermocouple introduced from the top (T.C. 18) with

others introduced from the sides (T.C. 4, 7 and 12) at the same bed location. Such a comparison is made in Table 14. Thermocouples 4 and 7 are compared with 18 at the shaft centerline while 12 is compared with 18 at the hot gas inlet since 12 was located inside the inlet. In all cases Thermocouple 18 indicated the higher temperature. The average difference between the temperatures measured by 4 and 18 was only 15°F which is the same magnitude as the calibration error for the thermocouples. The average temperature difference between 7 and 18 was 45°F while for 12 and 18 it was 149°F. The latter was large probably because of radiation from the protection tube containing Thermocouple 12 to the walls of the hot gas inlet which were very likely cooler than the gas.

Table 14. Comparison of temperatures measured by different thermocouples at shaft centerline

Run no.	Date	Time	Temperature, °F T.C. no. 18	T.C. no. 4	T.C. no. 7	T.C. no. 12	Temp. diff. °F
P-7	2-25-56	2235	1817	1806	-	-	11
P-7	2-26-56	1145	2080	2060	-	-	20
P-7	2-25-56	2250	1944	-	1890	-	54
P-7	2-26-56	1150	2131	-	2095	-	36
P-11-B	4-16-56	2230	2102[a]	-	-	1971[a]	131
P-11-B	4-17-56	1210	2076[a]	-	-	1910[a]	166

[a]Temperatures measured at hot gas inlet instead of shaft centerline.

Method of Operation

There were many variations in operating procedure because of equipment changes and because some operating techniques had to be developed before semicontinuous operation could be demonstrated. For example, the manner in which the bed was rodded proved to be the critical factor in keeping the solids free flowing. The method of operation described is that which finally evolved by trial and error and which was applied during the last few runs when the external combustion chamber was used and the furnace cover was left off to facilitate rodding.

To conserve the supply of sized gypsum the initial charge placed in the shaft furnace usually consisted of solids which were the product of previous runs and which had been passed over a screen with $\frac{1}{4}$ inch openings to remove fines. However, in the case of Run P-13 the bottom of the furnace was filled with -4 +6 mesh gypsum. In any case, the solids were added until the surface of the charge was about level with the hot gas inlet.

The flow of compressed air to the ejector was started to provide a furnace draft and firing was begun with low natural gas and air rates. These rates were gradually increased until the flows specified for the run were attained. Prior to Run P-13 the natural gas rate was generally the maximum which could be obtained with the available supply pressure. Some adjustments in the rates were always necessary to provide the desired concentrations of combustion products. Either during the period when the firing rate was being increased or afterwards, increments of 2 to 6 pounds of solids were added at about 30 minute intervals until the

bed depth (the distance from the hot gas inlet centerline to the surface of the charge) was about 12 inches.

After the charge had been heated up to the desired operating temperature and the proper air to natural gas ratio had been established, semicontinuous operation was started. Two different procedures were used; the first was based on maintaining a constant discharge rate, the second on a constant feed rate. The former was used for Runs P-10, P-11, and P-12, as follows: at 30 minute intervals the discharge screw was given one turn, the bed rodded, solids added, and the bed level measured. In rodding the bed a $\frac{1}{2}$ inch diameter steel rod was introduced at the top of the shaft and pushed down through the bed to the very bottom in about four places. For the first few hours of operation screened solids from former runs were sometimes added, followed by gypsum of the proper size. A reasonably constant bed depth was maintained by varying the size of the increments of gypsum. After every 5 to 7 revolutions of the discharge screw the solids which had collected in the storage chamber were withdrawn, weighed and sampled for subsequent analysis.

The procedure used for Run P-13, which was the final run, involved maintaining a constant feed rate. At 15 minute intervals the bed was rodded, 3 pounds of gypsum added, and the bed level measured. The steel rod was pushed down through the bed as before, but in only two places. At 5 or 6 minute intervals the discharge screw was given a single turn. The length of the interval was adjusted to keep the bed depth constant. After every 10 revolutions the solids were withdrawn from the storage chamber, weighed and sampled.

During semicontinuous operation it was possible to control the com-

position and flow rate of the gas entering the kiln, the character of the solids entering and the rate at which they passed through the kiln, and the bed depth or volume of solids exposed to the gas stream. Temperature, on the other hand, was difficult to measure and control. The gas piping between the combustion chamber and the bed of solids was designed to cool the gas so that it entered the solids at about the right temperature. But until the last run there was no way to correct changes in temperature which resulted from every change in gas composition or flow rate. During the final run some adjustment in temperature was possible through regulation of the rate of impingement of cooling air on the hot gas line.

At hourly intervals operating data were recorded, consisting of hot gas and furnace lining temperatures, natural gas and air flow rates, and bed pressure drop. At irregular intervals varying from a few minutes to several hours, depending on the stability of the operation, the hot gas entering the kiln was analyzed with an Orsat apparatus for carbon dioxide, oxygen and carbon monoxide. At rather infrequent intervals and when it was thought that a steady state had been reached, the off-gas was analyzed for sulfur dioxide. The off-gas sample was drawn at a reasonably constant rate of 100 milliliters per minute through a stainless steel tube inserted about 2 inches into the shaft through the opening provided for Thermocouple 4. Since it required at least 30 minutes to draw an off-gas sample, momentary fluctuations in composition were averaged out.

If a series of two or more runs was being made in the same operating period, the semicontinuous operation was continued throughout the series without pause and the end of one run and the beginning of the next was

marked only by the necessary changes in operating conditions. At the end of the series the operation was stopped and the solids remaining in the furnace were discharged in 4 to 7 pound increments. After each increment was drawn, the bed was rodded and the location of the bed surface measured. Each increment was weighed and sampled. All of the samples of the solids from the operation were subsequently analyzed for sulfide, sulfate, and calcium.

Methods of Analysis

The same methods were used for analyzing the solids which had passed through the shaft furnace as were used for analyzing the solids from the small scale laboratory experiments.

The gas was analyzed with an Orsat apparatus for carbon dioxide, oxygen, and carbon monoxide. Samples of gas taken from within the furnace were first scrubbed with a 50 per cent chromic acid solution and then with a solution of potassium dichromate in concentrated sulfuric acid before being analyzed by the Orsat method. This was to remove sulfur compounds which could interfere with the determination of carbon dioxide. When the gas was sampled between the combustion chamber and the kiln, scrubbing was unnecessary.

The sulfur dioxide in the furnace off-gas was estimated by an iodimetric method. An aspirator bottle was used to draw a large sample of gas through two washing bottles in series. The first bottle contained a standard iodine solution, which removed sulfur dioxide; the second contained a sodium hydroxide solution, which absorbed the carbon dioxide.

Nitrogen was collected in the aspirator bottle. Oxygen and carbon monoxide were generally negligible in amount. By drawing only enough gas to decolorize the iodine, a definite quantity of sulfur dioxide was absorbed and the volume of nitrogen associated with it could be measured in the aspirator bottle.

This method is not specific for sulfur dioxide since hydrogen sulfide will also react with iodine. However, the products of reaction are different as indicated by the following reactions:

$$SO_2 + I_2 + 2\ H_2O = 2\ HI + H_2SO_4 \qquad (34)$$

$$H_2S + I_2 = 2\ HI + S \qquad (35)$$

Thus sulfur is precipitated only if hydrogen sulfide is present. When the off-gas from the shaft furnace was analyzed, the iodine solution remained free of precipitates indicating that the concentration of hydrogen sulfide was negligible.

Results

Most of the work with the shaft furnace was directed toward demonstrating the equipment and developing a satisfactory operating procedure. Hence a sequence of runs was carried out in which variations in equipment and operating technique were investigated. Changes in the method of combustion and in the method of rodding the bed of solids proved to be the most important. In the beginning, combustion took place internally, that is within the bed interstices, and the bed was rodded through the holes in the sides of the furnace. An external combustion chamber was subse-

quently added and later the furnace was operated with its cover removed to enable rodding from the top.

Following the development of a satisfactory procedure a limited range of operating conditions was explored. Principally this involved observing the effect of changing the composition of the gas entering the bed from a neutral gas to a reducing gas containing small amounts of hydrogen and carbon monoxide.

The objectives sought, difficulties encountered, and results attained in individual runs are summarized in Table 15. A list of general operating conditions for the runs is presented in Table 16. Specific operating conditions such as temperature, gas flow rates, and actual gas compositions are not included in this table because they usually varied too much within runs. However, for the runs in which semicontinuous operation was successfully demonstrated specific operating conditions and results were plotted continuously for the entire run and are discussed in a later section.

The operation may be divided into three sections with respect to combustion location and method of rodding:

1. Internal combustion, furnace cover on, bed rodded from the sides, Runs P-1 through P-6.
2. External combustion, furnace cover on, bed rodded from the sides, Runs P-7 through P-9.
3. External combustion, furnace cover off, bed rodded from the top, Runs P-10 through P-13.

Table 15. Shaft furnace operation: objectives and difficulties

Run no. Date	Objectives of run	Operational difficulties	Objectives attained
P-1 9-12-55 to 9-13-55	Test general operability of kiln.	Charge got too hot. When air was admitted to cool charge, CaS was oxidized releasing more heat. Some clinkers were formed and several thermocouples failed.	Some operating characteristics determined.
P-2 9-16-55 to 9-17-55	(Same as above)	Centerline thermocouple failed twice.	(Same as above)
P-3 10-28-55 to 10-31-55	To attain simultaneously: 1. Neutral atmosphere 2. Uniform bed temperature 3. Semicontinuous operation	Centerline thermowell failed. Uniform bed temperature obtained by feeding all secondary air. Efficient combustion and neutral atmosphere not produced in this manner.	Uniform bed temperature during part of run.
P-4 11-22-55 to 11-26-55	(Same as above) To determine whether introducing natural gas at two different levels would produce a more uniform bed temperature.	Centerline thermowell failed. Gas composition could not be controlled within desired limits.	(Same as above)
P-5 12-17-55 to 12-19-55	(Same as above)	Gas composition and bed temperature could not be controlled within desired limits. Shaft became solidly plugged.	Semicontinuous operation for several hours until shaft plugged
P-6 1-1-56 to 1-3-56	(Same as above) To determine whether a lower bed depth would prevent plugging.	Gas composition and bed temperature could not be controlled within desired limits. Shaft became solidly plugged.	Semicontinuous operation for 28 hours before shaft plugged.
P-7 2-25-56 to 2-26-56	Test operation of external combustion chamber.	Natural gas pressure was inadequate in relation to the pressure drop between the combustion chamber and bed of solids.	Some operating characteristics of combustion chamber determined. Results showed composition of gas entering kiln could be controlled.
P-8 3-19-56 to 3-20-56	To attain semicontinuous operation.	Shaft appeared to be plugged after warm-up period and all efforts to move solids failed.	None

Table 15. (Continued)

Run no. Date	Objectives of run	Operational difficulties
P-9 3-20-56 to 3-21-56	To attain semicontinuous operation. To determine whether movement of bed from the very start would prevent plugging of shaft.	Solids packed until shaft solidly plugged. Run end from combustion chamber b Thermowell in this line a
P-10 4-13-56 to 4-15-56	To demonstrate semicontinuous operation for an extended period.	Solids packed until shaft plugged. Packing seemed over rodding the bed.
P-11-A 4-15-56 to 4-16-56	To demonstrate semicontinuous operation for an extended period. To determine extent of desulfurization and CaS formation for given conditions.	None
P-11-B 4-16-56 to 4-17-56	(Same as above)	None
P-12-A 5-18-56 to 5-19-56	To determine extent of desulfurization and CaS formation for given conditions. To test hot gas distributor.	None
P-12-B 5-19-56 to 5-20-56	(Same as above)	Hot gas distributor disin
P-12-C 5-20-56 to 5-21-56	To determine extent of desulfurization and CaS formation for given conditions.	None
P-13 5-14-58 to 5-16-58	To determine extent of desulfurization and CaS formation for given conditions. To test metal-ceramic hot gas distributor.	None

Operational difficulties	Objectives attained
ids packed until shaft was almost idly plugged. Run ended when pipe m combustion chamber burned through. rmowell in this line also failed.	Semicontinuous operation for several hours.
ids packed until shaft was solidly gged. Packing seemed to be due to r rodding the bed.	Semicontinuous operation was maintained without difficulty for 26 hours before shaft started plugging.
e	Semicontinuous operation demonstrated. For extent of desulfurization and CaS formation see Figure 50.
e	(Same as above)
e	For extent of desulfurization and CaS formation see Figure 51.
gas distributor disintegrated.	(Same as above)
e	(Same as above)
e	For extent of desulfurization and CaS formation see Figure 52. Hot gas distributor survived.

Table 16. Shaft furnace: general operating conditions

Run no. Date	Duration hours	Cover position	Initial charge	Solids added during run	So
P-1 9-12-55 to 9-13-55	20 (warm-up included)	On	Filled with -1/2 +3/8 in. gypsum.	None	Non
P-2 9-16-55 to 9-17-55	34 (warm-up included)	On	Filled with -1/2 +3/8 in. gypsum.	None	Non
P-3 10-28-55 to 10-31-55	80 (warm-up included)	On	Filled with -1/2 +3/8 in. gypsum.	-1/2 +3/8 in. gypsum to make up for bed shrinkage.	Non
P-4 11-22-55 to 11-26-55	85 (warm-up included)	On	Filled with screened solids from previous runs.	-1/2 +3/8 in. gypsum to make up for bed shrinkage.	Non
P-5 12-17-55 to 12-19-55	48 (warm-up included)	On	Filled with screened solids from previous runs.	-1/2 +3/8 in. gypsum added at varying intervals of time.	1 of per hou
P-6 1-1-56 to 1-3-56	50 (warm-up included)	On	60% filled with screened solids from previous runs.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 of per hou
P-7 2-25-56 to 2-26-56	27 (warm-up included)	On	Filled with screened solids from previous runs.	None	No
P-8 3-19-56 to 3-20-56	21 (warm-up included)	On	Filled to 5 in. bed depth with screened solids from previous run.	-1/2 +3/8 in. gypsum added to increase bed depth to 18 in.	Al
P-9 3-20-56 to 3-21-56	12	On	Filled to gas inlet with screened solids from previous run.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 of

Solids added during run	Solids discharged during run	Combustion location	Type of atmosphere
None	None	Internal	Probably reducing
None	None	Internal	Probably reducing
-1/2 +3/8 in. gypsum to make up for bed shrinkage.	None	Internal	Varied
-1/2 +3/8 in. gypsum to make up for bed shrinkage.	None	Internal	Varied
-1/2 +3/8 in. gypsum added at varying intervals of time.	1 lb. at intervals of 30 min. for a period of about 14 hours.	Internal	Varied
-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min. for a period of about 28 hours.	Internal	Varied
None	None	External	Varied
-1/2 +3/8 in. gypsum added to increase bed depth to 18 in.	Almost none	External	Almost neutral
n- -1/2 +3/8 in. ed gypsum added at - 30 min. intervals.	1 lb. at intervals of 30 min.	External	Almost neutral

Table 16. (Continued)

Run no. Date	Duration hours	Cover position	Initial charge	Solids added during run	
P-10 4-13-56 to 4-15-56	31	Off	Filled to 4 in. below gas inlet with screened solids from previous run.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 c
P-11-A 4-15-56 to 4-16-56	30	Off	Filled to gas inlet with screened solids from previous	Screened solids from previous run added at 30 min. intervals for first 3 hr. Then -1/2 +3/8 in. gypsum added at 30 min. intervals.	1 c
P-11-B 4-16-56 to 4-17-56	17	Off	Operation continued from P-11-A without interruption.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	
P-12-A 5-18-56 to 5-19-56	18	Off	Filled to gas inlet with screened solids from previous	Screened solids from previous run added at intervals for about first 4 hrs. Then -1/2 +3/8 in. gypsum added at 30 min. intervals.	
P-12-B 5-19-56 to 5-20-56	25	Off	Operation continued from P-12-A without interruption.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	
P-12-C 5-20-56 to 5-21-56	14	Off	Operation continued from P-12-B without interruption.	-1/2 +3/8 in. gypsum added at 30 min. intervals.	
P-13 5-14-58 to 5-16-58	50	Off	Filled to 2 in. below gas inlet with -4 +6 mesh gypsum.	3 lb. of -3/4 +1/2 in. gypsum added at 15 min. intervals.	

Solids added during run	Solids discharged during run	Combustion location	Type of atmosphere
-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Neutral
Screened solids from previous run added at 30 min. intervals for first 3 hr. Then -1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Neutral
-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Reducing (1% CO) (1% H_2)
Screened solids from previous run added at intervals for ~~about first~~ 4 hrs. Then -1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Slightly oxidizing
-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Reducing (1% CO) (1% H_2)
-1/2 +3/8 in. gypsum added at 30 min. intervals.	1 lb. at intervals of 30 min.	External	Reducing (2% CO) (2% H_2)
3 lb. of -3/4 +1/2 in. gypsum added at 15 min. intervals.	0.5 lb. at 5 to 8 min. intervals.	External	Reducing (2% CO) (2% H_2)

Internal combustion, furnace cover on

The early runs involved a study of factors affecting combustion within the bed. The ratios of primary and secondary air to natural gas and the location of one gas inlet nozzle were varied in an attempt to secure a uniform bed temperature distribution and controlled off-gas composition. More specifically a neutral off-gas, that is one having negligible concentrations of either oxygen or reducing gases, was sought. Feeding only premixed air and natural gas produced localized, very hot zones near the gas inlet nozzles, while feeding air and natural gas separately tended to produce a broad zone of uniform temperature. However, feeding all secondary air did not promote good mixing of natural gas and air so the combustion was inefficient. Various combinations of primary and secondary air sometimes produced relatively uniform bed temperatures but the off-gas composition could not be closely controlled.

The main objective for the last two runs in this section was the establishment of semicontinuous operation while control of off-gas composition and a uniform bed temperature were considered secondary objectives. Intermittent withdrawal of solids and feeding of gypsum began without incident but almost immediately large fluctuations in both bed temperature and off-gas composition began taking place. It was noticed that if the bed was not thoroughly rodded after each withdrawal hollow spots developed where combustion concentrated and caused local overheating. As the semicontinuous operation progressed, the operation became more and more unsteady and gradually the bed offered increasing resistance to rodding. Eventually the point was reached where the solids were so tightly packed that the shaft was solidly plugged. By then very little combustion took

place within the bed and the gas was observed burning above the bed. Operation was then discontinued and the furnace unloaded.

An example of the plugging which occurred is shown in Figure 49. The plug shown remained in the upper part of the shaft after the furnace was unloaded following Run P-5. It was about 15 inches thick and did not break loose even after the large hole which appears in the picture was punched through. The particles did not appear to be cemented or fused together but they ranged in size from fine powder up to feed size. The fines filled the interstices between the larger particles, leaving little space for gas flow or for combustion. The large quantity of fines was produced by rodding the dehydrated gypsum which was extremely friable.

Generally the solids from this series of runs contained a high percentage of calcium sulfate. Many of the samples also contained considerable calcium sulfide, while calcium oxide, the desired product, was usually present in the least amount.

External combustion, furnace cover on

Since the composition of the gas passing through the furnace could not be adequately controlled when natural gas was burned within the bed, combustion in an external chamber was tried. It was found that the composition of the gas from the combustion chamber could be controlled within reasonable limits. By varying the ratio of air to natural gas either an oxidizing, neutral or reducing gas could be produced. For example, it was possible to supply the kiln with a hot gas containing negligible amounts of oxygen and reducing gases or with one containing a negligible amount of oxygen and up to several per cent each of carbon monoxide and

Figure 49. Shaft plugged with solids

hydrogen. Since hydrogen was not analyzed for, its concentration was assumed to be the same as that of carbon monoxide in accordance with the findings of the American Gas Association Committee on Industrial Gas Research (1).

During this series of runs the hot gas entering the furnace was usually neutral in composition. The solids discharged from the furnace generally had a large proportion of calcium sulfate and a small amount of calcium oxide but very little calcium sulfide.

Although the use of an external combustion chamber solved one difficulty, the problem of the shaft plugging remained. It was apparently easy to compact the bed to the point where the solids would no longer flow. In rodding the bed from the sides it was difficult to judge what was happening to the solids. Therefore in the next sequence of runs the furnace cover was removed to permit rodding from the top.

External combustion, furnace cover off

In Run P-10 semicontinuous operation proceeded smoothly for more than 26 hours with moderate rodding of the bed from the top. Then by rodding the bed excessively the solids were packed little by little until the shaft was plugged. It was demonstrated in subsequent runs that the solids would remain free flowing and semicontinuous operation could be continued indefinitely if the bed were rodded by pushing a $\frac{1}{2}$ inch diameter steel rod down through it in about four places after each withdrawal of solids.

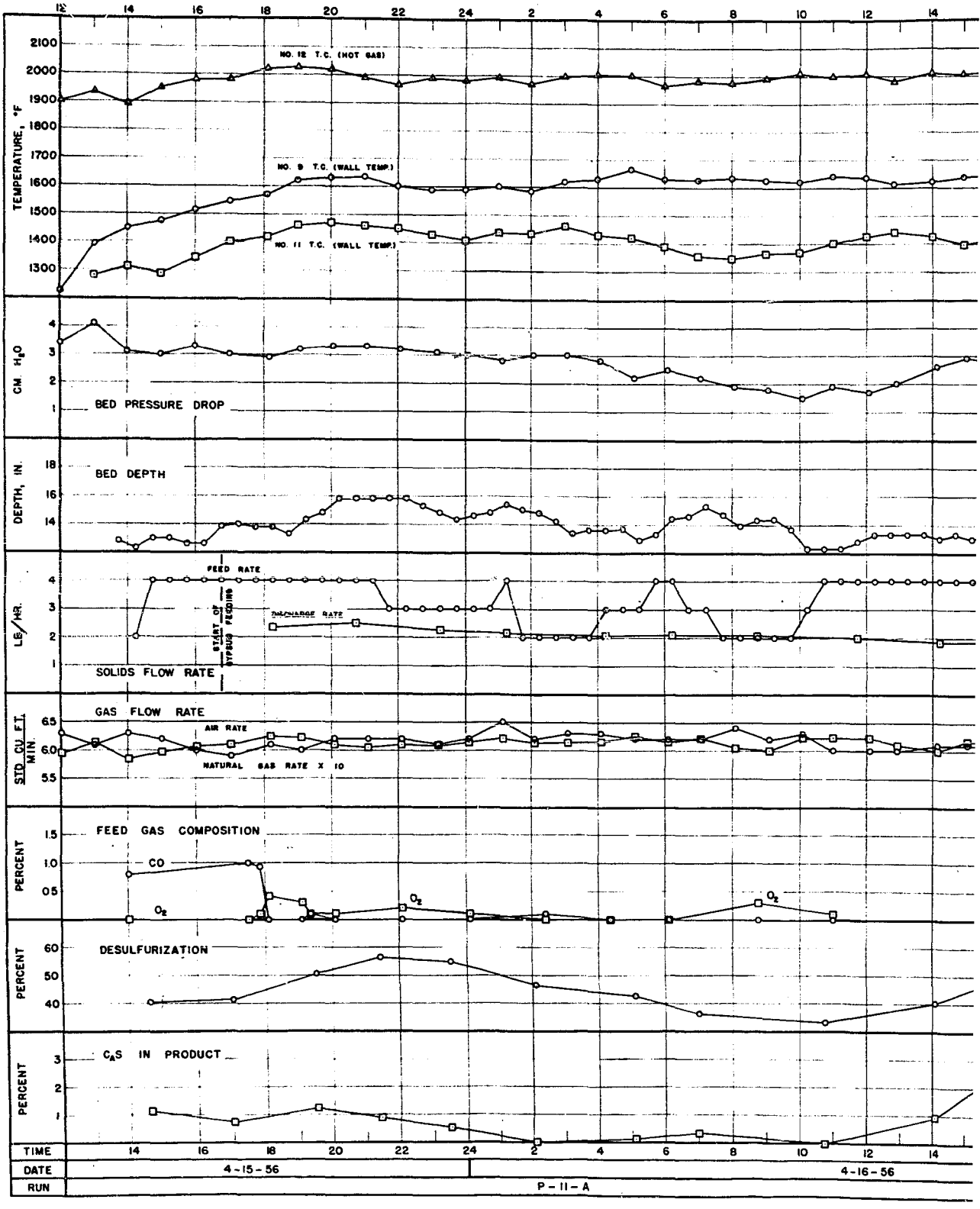
The procedure for semicontinuous operation proved satisfactory in Run P-11-A and subsequent runs. Consequently it was possible to operate the furnace with reasonably constant conditions for relatively long

periods. Run P-11-A was carried out with operating conditions set to give a nominally neutral hot gas. After about 30 hours of operation the air feed rate was reduced slightly to provide 1 per cent carbon monoxide and 1 per cent hydrogen in the hot gas and Run P-11-B was carried out for a period of about 17 hours. Before the P-12 series of runs a distributor for the hot gas was installed in the furnace. Conditions were established which provided an approximately neutral hot gas and Run P-12-A was carried out over a period of about 18 hours. This was followed by Run P-12-B with a 2 per cent nominal concentration of reducing gases and Run P-12-C with 4 per cent.

Although the mechanical operation of the shaft furnace was satisfactory, in general the desulfurization was too low and the per cent calcium sulfide in the by-product too high in these two series of runs. The maximum desulfurization was realized during Run P-12-B and it amounted to 78 per cent. At the same time the by-product had 13 per cent calcium sulfide. The minimum desulfurization (30 per cent) and the maximum calcium sulfide (35 per cent) were obtained during Run P-12-C when the carbon monoxide concentration was greatest. For a relatively neutral hot feed gas the calcium sulfide approached a negligible value but the desulfurization was only 35 or 40 per cent. These are not average values and they probably do not represent values which would be obtained under steady state conditions because the runs were too short in duration. When the results were plotted in Figures 50 and 51, it was evident that sufficient time had not been allowed to insure steady state operation.

In Figures 50 and 51 the operating conditions and results for the P-11 and P-12 series respectively are shown. The time used for plotting

Figure 50. Hourly operating conditions and results for the P-11 series of runs


TEMPERATURE, °F
NO. 12 T.C. (HOT GAS)
NO. 9 T.C. (WALL TEMP.)
NO. 11 T.C. (WALL TEMP.)
CM. H2O
BED PRESSURE DROP
DEPTH, IN.
BED DEPTH
LB/HR.
FEED RATE
START OF BYPASS FEEDING
DISCHARGE RATE
SOLIDS FLOW RATE
STD. CU. FT. MIN.
GAS FLOW RATE
AIR RATE
NATURAL GAS RATE X 10
PERCENT
FEED GAS COMPOSITION
CO
O2
DESULFURIZATION
CaS IN PRODUCT
TIME
DATE
RUN
4-15-56
4-16-56
P-11-A

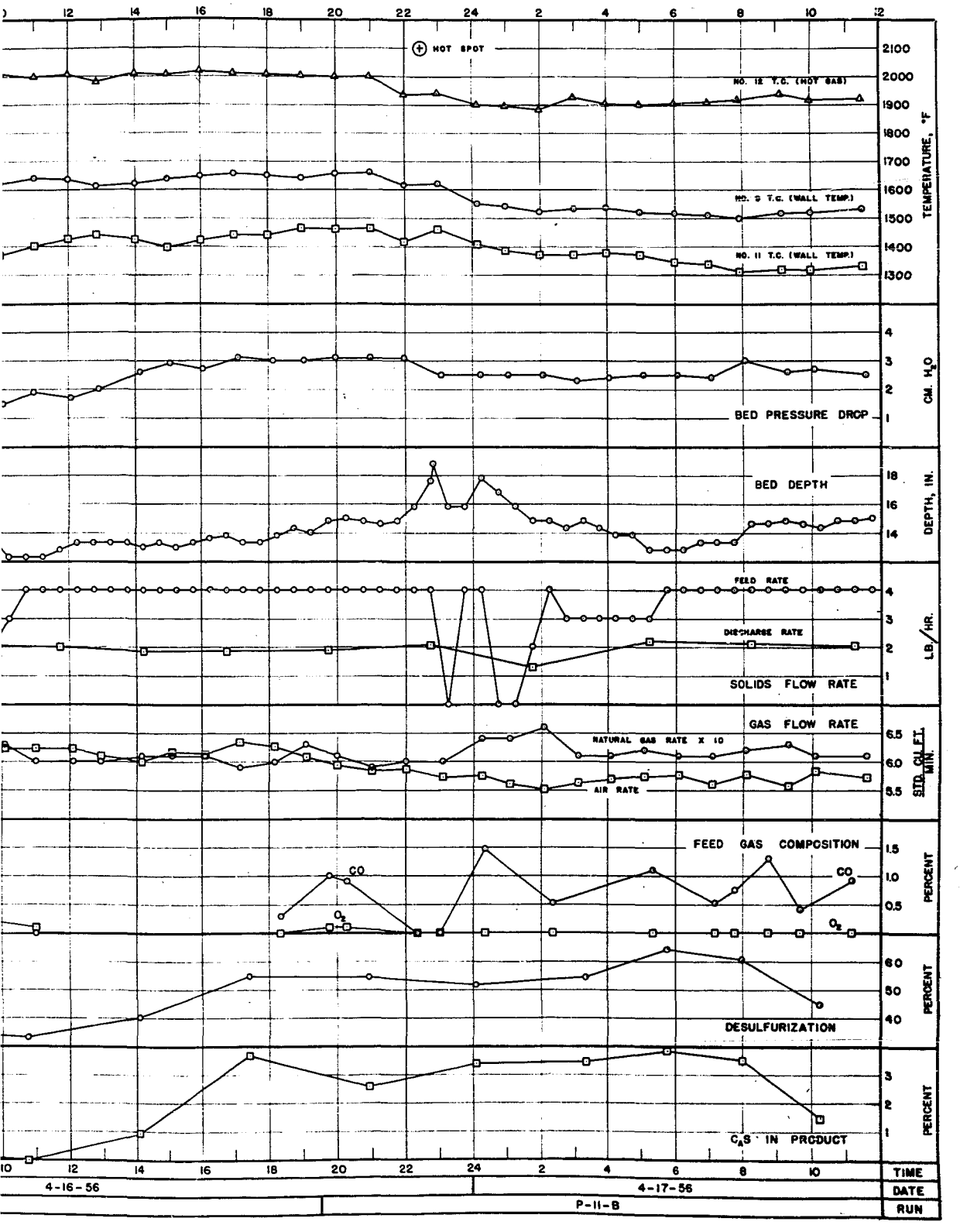
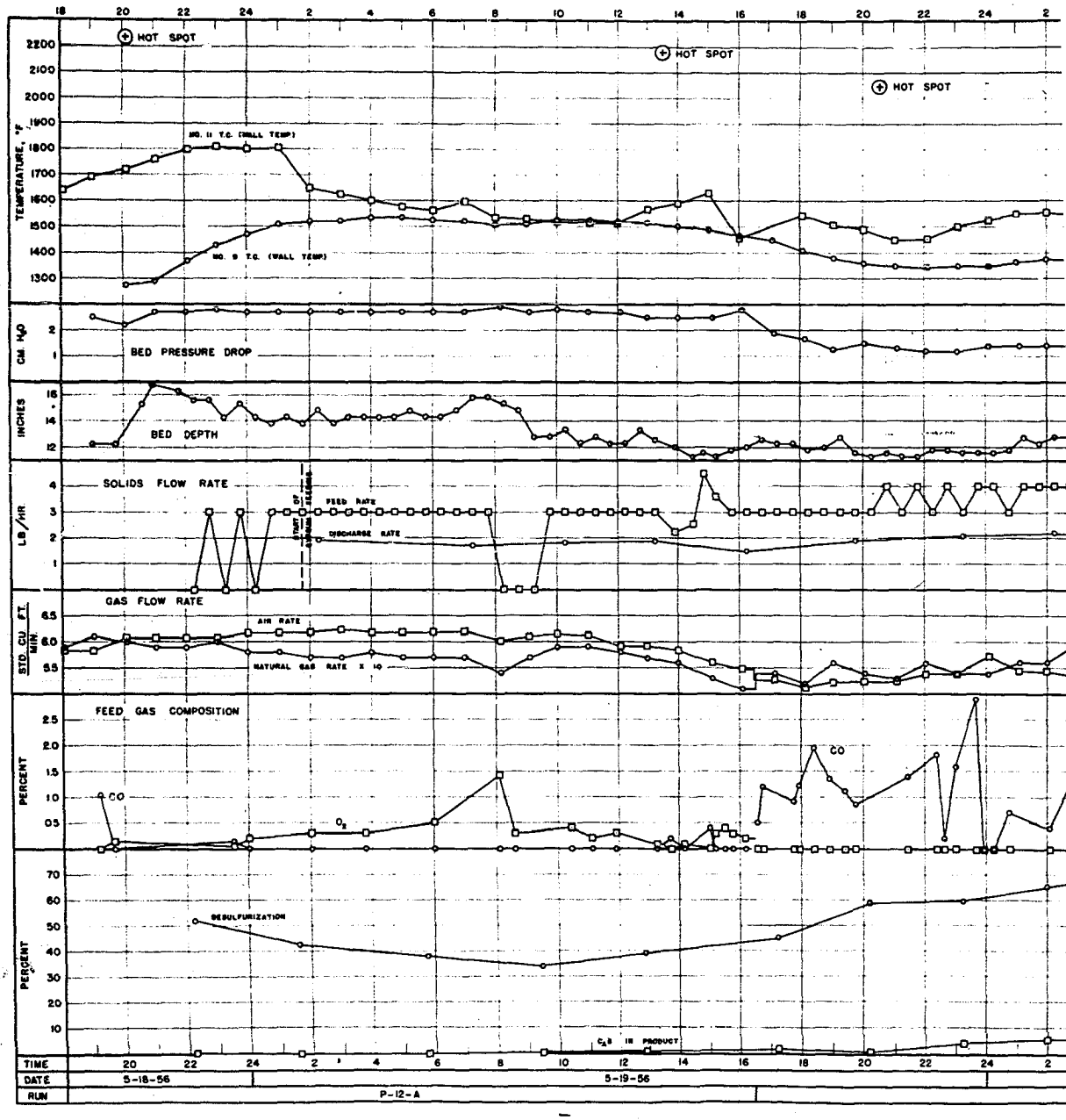
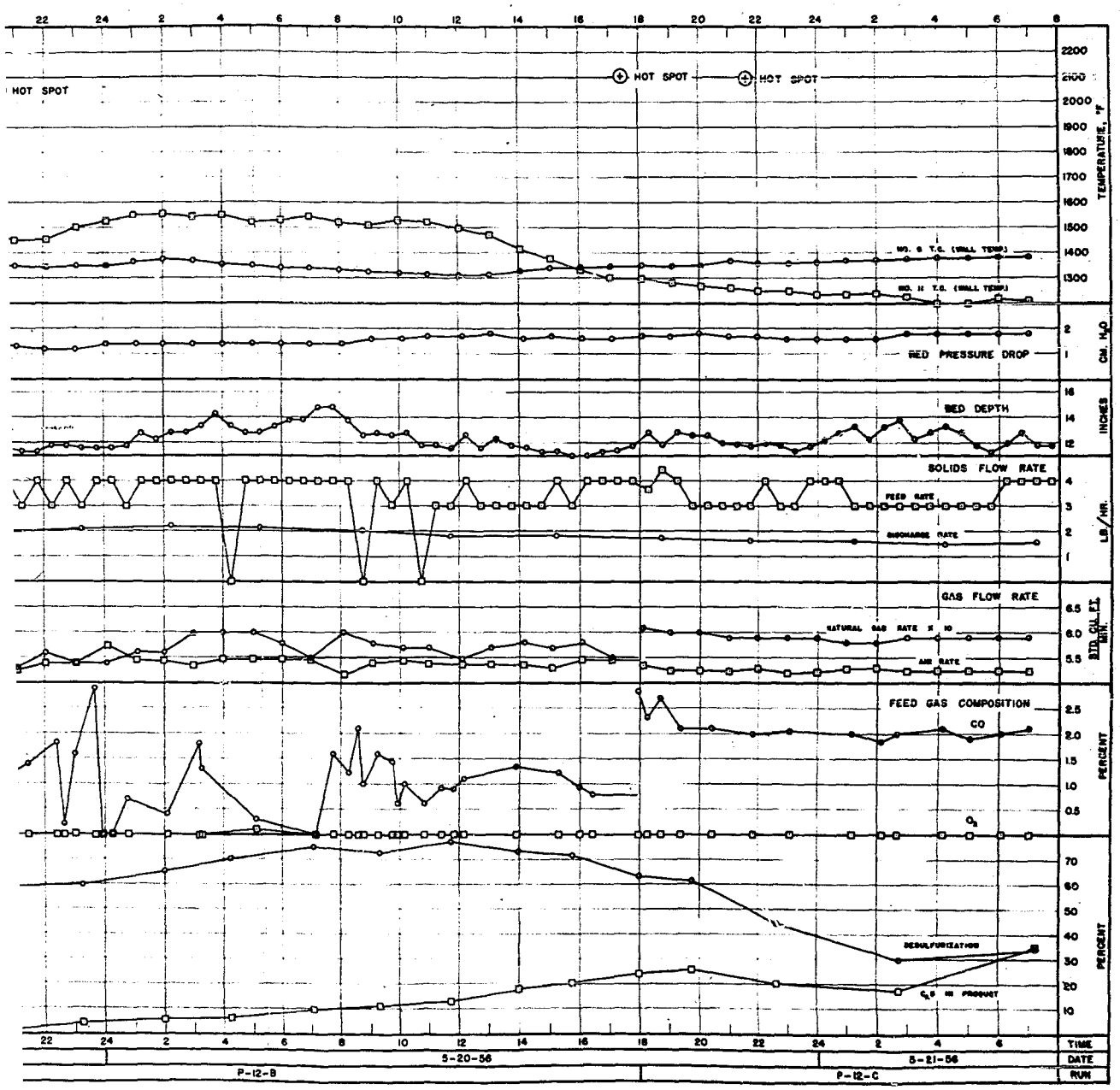

12 14 16 18 20 22 24 2 4 6 8 10 12
HOT SPOT
NO. 12 T.C. (HOT GAS)
NO. 9 T.C. (WALL TEMP.)
NO. 11 T.C. (WALL TEMP.)
2100 2000 1900 1800 1700 1600 1500 1400 1300
TEMPERATURE, °F
BED PRESSURE DROP
4 3 2 1
CM. H2O
BED DEPTH
18 16 14
DEPTH, IN.
FEED RATE
DISCHARGE RATE
SOLIDS FLOW RATE
4 3 2 1
LB./HR.
GAS FLOW RATE
NATURAL GAS RATE X 10
AIR RATE
6.5 6.0 5.5
STD. CU. FT. MIN.
FEED GAS COMPOSITION
CO
O2
1.5 1.0 0.5
PERCENT
DESULFURIZATION
60 50 40
PERCENT
CAS IN PRODUCT
3 2 1
PERCENT
10 12 14 16 18 20 22 24 2 4 6 8 10
TIME
4-16-56
4-17-56
DATE
P-11-B
RUN

Figure 51. Hourly operating conditions and results for the P-12 series of runs


HOT SPOT
HOT SPOT
HOT SPOT
TEMPERATURE, °F
NO. 11 T.C. (WALL TEMP)
NO. 9 T.C. (WALL TEMP)
CM. H2O
BED PRESSURE DROP
INCHES
BED DEPTH
LB./HR.
SOLIDS FLOW RATE
FEED RATE
DISCHARGE RATE
STD. CU. FT. / MIN.
GAS FLOW RATE
AIR RATE
NATURAL GAS RATE X 10
PERCENT
FEED GAS COMPOSITION
CO
O2
CO
PERCENT
DESULFURIZATION
C4S IN PRODUCT
TIME
DATE
5-18-56
5-19-56
RUN
P-12-A


HOT SPOT
HOT SPOT
HOT SPOT
TEMPERATURE, °F
NO. 9 T.C. (WALL TEMP.)
NO. 11 T.C. (WALL TEMP.)
BED PRESSURE DROP
CM. H2O
BED DEPTH
INCHES
SOLIDS FLOW RATE
FEED RATE
DISCHARGE RATE
LB/HR.
GAS FLOW RATE
NATURAL GAS RATE X 10
AIR RATE
STD. CU. FT. MIN.
FEED GAS COMPOSITION
CO
O2
PERCENT
DESULFURIZATION
C4 IN PRODUCT
PERCENT
TIME
DATE
RUN
5-20-56
5-21-56
P-12-B
P-12-C

the per cent desulfurization and per cent calcium sulfide was that when the solids were estimated to be in the reaction zone. This could be estimated only roughly due to the large lag between the time an increment of solids was in the reaction zone and the time when it was discharged and sampled.

To obtain the gypsum feed rate the weight of an added increment of gypsum was divided by the time interval between additions. For most of these runs the average feed rate was 3.4 pounds per hour. Run P-12-A was the exception with a feed rate of 2.7 pounds per hour. The solids discharge rate was obtained in a similar manner.

The "hot spot" temperature plotted in Figure 50 was measured in the bed next to the hot gas inlet with Thermocouple 18. The "hot spot" temperatures in Figure 51 were the maximum bed temperatures measured along a vertical line located 1 inch south of the shaft centerline. They were not necessarily the highest bed temperatures. In the P-12 series of runs the hot gas distributor used did not leave room for Thermocouple 12 so the hot gas temperature could not be measured.

As long as no excess air was being fed, reducing the air to natural gas ratio had the effect of increasing the concentration of reducing gases and also of decreasing the temperature of the hot gas leaving the combustion chamber. Thus the change in the air to natural gas ratio between Run P-11-A and P-11-B caused a drop of 80 to 100°F in hot gas temperature. The two furnace lining temperatures measured by Thermocouples 9 and 11 also dropped accordingly.

Both the per cent desulfurization and concentration of calcium sulfide in the by-product were greater for Run P-11-B than for P-11-A.

Since both the temperature and composition of the hot gas changed from one run to the next, the results could not be attributed directly to either variable. From kinetic and thermodynamic considerations, though, it would be expected that a decrease in temperature would cause a decrease in the degree of desulfurization, whereas an increase in concentration of reducing gases might cause an increase in desulfurization. Consequently the increase produced in the per cent desulfurization in going from the conditions of Run P-11-A to those of P-11-B was probably caused by the increase in reducing gas concentration. On the other hand, both an increase in the concentration of reducing gases and a decrease in the temperature would promote an increase in the percentage of calcium sulfide.

The P-12 series of runs was complicated by the disappearance of the hot gas distributor. Pieces of scale found in the discharged solids indicated that the distributor probably disintegrated between 2:00 and 8:00 P.M. on May 20, 1956. During the same interval the temperature measured by Thermocouple 11 dropped and that measured by Thermocouple 9 increased, which tended to confirm this inference. Therefore, it was probable that the distributor lasted through Run P-12-A and most of P-12-B.

During the P-12 series maximum desulfurization was obtained during Run P-12-B while operating with nominal concentrations of 1 per cent carbon monoxide and 1 per cent hydrogen in the hot gas. The absence of reducing gases in Run P-12-A probably caused the smaller desulfurization there. On the other hand, the reason for the lower desulfurization in Run P-12-C was not apparent. It might have been due in part to the disintegration of the hot gas distributor and in part to a lower hot gas

temperature brought about by the reduced air to natural gas ratio.

Although the hot gas distributor seemed to cause little difference between the results of Runs P-11-A and P-12-A, it did seem to increase the degree of desulfurization between Runs P-11-B and P-12-B. A maximum of 78 per cent desulfurization was obtained in Run P-12-B as compared with a maximum of 64 per cent in Run P-11-B. Except for the distributor and greater variation in the hot gas composition during Run P-12-B, conditions were approximately the same for both runs.

The most successful semicontinuous operation of the shaft furnace was realized during Run P-13 which was continued for 49 hours. The operation was smooth and relatively constant conditions were maintained. No mechanical breakdowns occurred.

In this run -3/4 +½ inch size gypsum was fed at a rate of 12 pounds per hour. The average desulfurization was 85 per cent and the average concentration of calcium sulfide in the by-product was 2.2 per cent. Based on the average percentage desulfurization, the estimated concentration of sulfur dioxide in the off-gas was 2.7 per cent. During the last 7 hours these quantities increased to 89 per cent desulfurization, 3.1 per cent calcium sulfide and 2.8 per cent sulfur dioxide.

The improved operation was the result of equipment modifications and changes in operating conditions. The gypsum feed rate was 3.5 times as large and the hot gas rate about twice as large as for the preceeding runs. The reactants were introduced in approximately stoichiometric proportions. In addition, the hot gas was introduced near the shaft centerline at a higher temperature. An increased natural gas supply pressure and a new transfer line from the combustion chamber made possible the

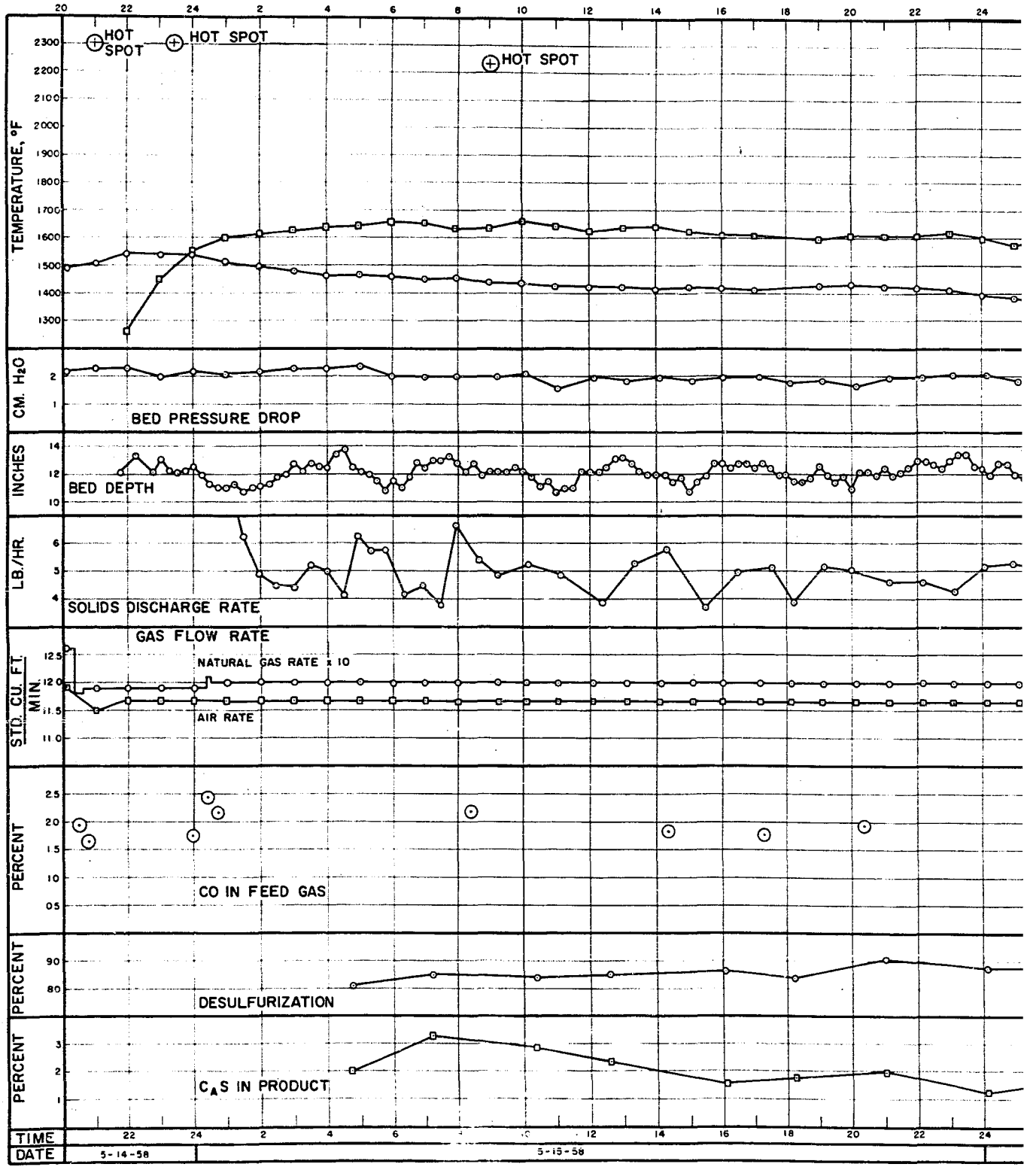
higher gas flow rate and higher temperature respectively. The hot gas distribution should have been better than for any previous runs with the possible exception of Runs P-12-A and P-12-B.

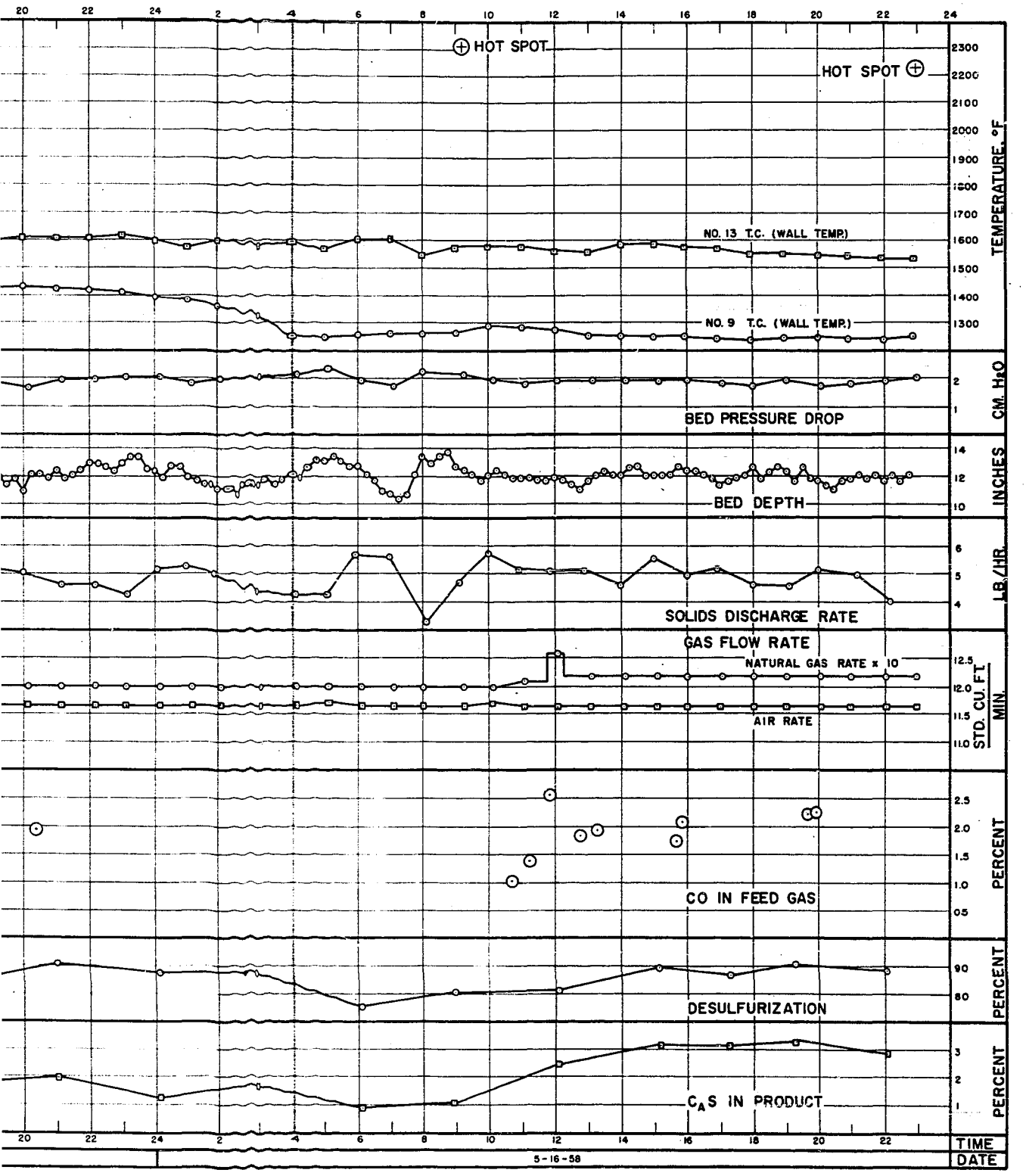
The hour to hour operating conditions and results are plotted in Figure 52. An attempt was made to keep the gypsum feed rate, bed depth, air rate, carbon monoxide concentration, and hot spot temperature constant. The natural gas rate was adjusted to give as close to 2 per cent carbon monoxide in the hot gas as possible. With the exception of a few hours, operation conditions were kept fairly uniform. Between 2:00 and 4:00 A.M. on May 16, the per cent desulfurization, per cent calcium sulfide, and temperature measured by Thermocouple 9 all dropped. This was apparently due to a reduction in the carbon monoxide concentration which went unobserved for several hours because of a gap in gas analyses. The carbon monoxide concentration may have decreased because of a change in the natural gas composition.

The "hot spot" temperature recorded in Figure 52 was determined by inserting a protected thermocouple into the bed from the top so that the thermocouple was located slightly below the hot gas inlet and near the shaft centerline. This temperature seemed to pass through a cycle which corresponded with the periodic additions of gypsum and bed rodding. A maximum temperature, which was probably near the temperature of the entering hot gas, was reached just before an increment of gypsum was added and the bed rodded. This is the one reported.

Several times during the run the concentration of sulfur dioxide in the off-gas was determined. By combining these values with the results of Orsat analyses and the specified natural gas composition furnished by

Figure 52. Hourly operating conditions and results for Run P-13


TEMPERATURE, °F
HOT SPOT
HOT SPOT
HOT SPOT
CM. H2O
BED PRESSURE DROP
INCHES
BED DEPTH
LB./HR.
SOLIDS DISCHARGE RATE
GAS FLOW RATE
STD. CU. FT. MIN.
NATURAL GAS RATE x 10
AIR RATE
PERCENT
CO IN FEED GAS
PERCENT
DESULFURIZATION
PERCENT
CA S IN PRODUCT
TIME
DATE
5-14-58
5-15-58


20 22 24 2 4 6 8 10 12 14 16 18 20 22 24
HOT SPOT
HOT SPOT
NO. 13 T.C. (WALL TEMP.)
NO. 9 T.C. (WALL TEMP.)
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
TEMPERATURE, °F
BED PRESSURE DROP
2
1
CM. H₂O
BED DEPTH
14
12
10
INCHES
SOLIDS DISCHARGE RATE
6
5
4
LB./HR.
GAS FLOW RATE
NATURAL GAS RATE x 10
AIR RATE
12.5
12.0
11.5
11.0
STD. CU. FT. / MIN.
CO IN FEED GAS
2.5
2.0
1.5
1.0
0.5
PERCENT
DESULFURIZATION
90
80
PERCENT
C_AS IN PRODUCT
3
2
1
PERCENT
20 22 24 2 4 6 8 10 12 14 16 18 20 22
TIME
5-16-58
DATE

the supplier, it was possible to estimate the off-gas composition. The values obtained are listed in Table 17. For comparison the concentration of sulfur dioxide calculated from the per cent desulfurization is also included. Although the observed concentrations of sulfur dioxide were noticeably lower in the first three instances, there was good agreement between the observed and calculated values in the last two cases.

Table 17. Composition of off-gas during Run P-13

Date	Time	Off-gas composition, mole %: By gas analysis N_2	H_2O[b]	CO_2	SO_2	Calculated[a] SO_2
5-15-58	1402-1430	70.8	17.4	9.4	2.4	2.7
5-15-58	2015-2052	70.9	17.3	9.4	2.4	2.8
5-16-58	1039-1118	71.5	17.2	9.3	2.1	2.6
5-16-58	1530-1600	70.5	17.4	9.4	2.7	2.8
5-16-58	1948-2009	70.2	17.5	9.5	2.9	2.9

[a]Calculated from per cent desulfurization of gypsum.

[b]Estimated from average natural gas composition.

Discussion of Results

The pilot plant demonstration of a shaft furnace process for desulfurizing gypsum was carried to the point where mechanical feasibility was shown. This required developing an operating technique as well as modifying the original equipment. It was found necessary to rod the bed of solids to prevent arching, but excessive rodding compacted the bed and plugged the shaft. In order to provide the carefully controlled atmosphere required for reductive decomposition it was found that natural gas had to be burned in a separate combustion chamber rather than within the bed of solids.

After a satisfactory method of operation had been developed and the equipment appropriately modified, a relatively long demonstration run (P-13) was made. In choosing the operating conditions consideration was given to the results of the laboratory investigation as well as to the results of the previous shaft furnace operation. The following conditions were selected:

hot feed gas, 2% CO, 2% H_2 (assumed)

maximum bed temperature, 2300°F

gypsum size, -3/4 +½ inch

gypsum feed rate, 12 lb./hr.

$(CO + H_2)/CaSO_4 = 1.0$

The resulting gas mass velocity was 0.075 pounds per second per square foot. This was a lower mass velocity than was used in the laboratory investigation but further changes in equipment would have been needed to obtain a higher rate.

The best results were obtained in the final 7 hours of Run P-13. The gypsum was 89 per cent desulfurized and an off-gas containing 2.8 per cent sulfurous gases and a by-product lime containing 3.1 per cent calcium sulfide were produced. This concentration of sulfurous gases seems rather low for converting into sulfuric acid while the per cent calcium sulfide is probably too high for a marketable lime. Hence, the results do not indicate that the process is economically feasible. However, it was unlikely that optimum conditions were employed, so further improvement in results is possible.

In addition, the laboratory results indicated that reductive decomposition must be carried out within a temperature range of about 100°F, which is a relatively narrow range at the temperature level involved. It would be difficult to operate a shaft furnace to provide the required temperature uniformity. On the other hand, a fluidized bed reactor could provide the narrow temperature range required.

CONCLUSIONS

1. Thermal decomposition does not seem to be a practical method for the desulfurization of gypsum. The application of thermal decomposition is probably limited by the equilibrium and not the rate of decomposition.
2. Reductive decomposition in which a reducing gas such as carbon monoxide or hydrogen in low concentration is passed over heated gypsum seems to be both thermodynamically and kinetically feasible.
3. The optimum temperature for reductive decomposition is in the range of 2200 to 2250°F.
4. Either carbon dioxide or water vapor can be mixed with the reducing gas to inhibit the formation of calcium sulfide.
5. Hydrogen results in faster decomposition rates than carbon monoxide, apparently without any greater tendency to produce calcium sulfide.
6. The desulfurization rate is affected by the temperature, mass velocity, particle size, and feed gas composition. Under special conditions the following seem to hold:
   a. The maximum desulfurization rate reaches a peak value between 2150 and 2250°F, depending on the gas composition.
   b. The maximum desulfurization rate increases but the initial desulfurization rate decreases as the gas mass velocity is increased.
   c. The maximum desulfurization rate increases but the initial desulfurization rate is unaffected as the particle size is reduced.

d. The desulfurization rate increases lineally with carbon monoxide concentration.

e. The maximum desulfurization rate decreases slightly with increasing concentrations of carbon dioxide.

f. The initial desulfurization rate is reduced by the presence of sulfur dioxide. Concentrations as low as 0.5 per cent are effective.

7. The conversion of gypsum to calcium sulfide is favored by reducing the temperature, increasing the concentration of carbon monoxide, and reducing the concentration of carbon dioxide. The presence of sulfur dioxide also favors the formation of calcium sulfide.

8. Mechanical operation of the shaft furnace used for desulfurizing gypsum was shown to be satisfactory.

9. It was demonstrated that gypsum can be at least 89 per cent desulfurized in a shaft furnace while producing an off-gas containing 2.8 per cent sulfurous gases and a by-product lime containing 3.1 per cent calcium sulfide.

10. Economic feasibility of the shaft furnace process was not shown. However, since the optimum operating conditions were not completely determined, further improvement is possible.

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APPENDIX

Table 18. Results of desulfurization rate investigation using -7+8 mesh particles of gypsum

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
3	A	1.50	23.4[c]	0.214	- 0.5 O_2 -	2090	2090	-	17.9	0.12	0.12
4	A	1.50	25.8[c]	0.107	- 0.6 O_2 -	2260	2260	-	98.4	0.79	0.79
5	B	1.38	28.1[c]	0.110	- 0.4 O_2 -	2210	2210	-	97.3	0.79	0.79
6	A	1.63	27.3[c]	0.107	- - -	2240	2240	-	99.4	1.52	1.52
7	B	1.38	28.9[c]	0.106	- - -	2260	2260	-	60.7	1.52	1.52
8	D	1.38	23.5[c]	0.108	- - -	-	-	-	99.7	-	-
9	C	1.56	25.5[c]	0.216	- 0-0.4 O_2 -	-	-	-	53.7	-	-
10	C	1.56	26.5[c]	0.216	- - -	-	-	-	75.2	-	-
11	C	1.56	25.3[c]	0.218	- - -	2240	2270	-	96.2	1.54	2.12
13	D	1.38	23.2[c]	0.218	- - -	-	-	-	97.1	-	-
14	F	0.75	14.6[c]	0.098	- - -	2310	2310	-	97.5	4.81	4.81
15	G	0.75	13.0[c]	0.106	- - -	2300	2300	-	62.0	2.90	2.90

[a]Temperatures correspond to initial and maximum desulfurization rate periods.

[b]Remainder nitrogen.

[c]-6+8 mesh

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
16	E	1.56	24.7[c]	0.236	- - -	2230	2230	-	38.2	1.76	1.76
17	F	0.75	15.1[c]	0.109	- - -	2260	2260	-	98.5	2.33	2.33
18	E	1.00	14.2	0.248	- - -	2240	2240	-	96.2	2.15	2.15
19	I	1.00	18.7	0.212	- - -	2270	2270	-	96.8	2.71	2.71
20	F	1.00	19.7	0.116	2.0 H_2 - -	2250	2250	13.85	87.2	6.54	6.54
21	G	1.00	14.1	0.115	3.9 H_2 - -	2160	2160	27.2	73.8	12.43	12.43
22	F	1.00	18.3	0.228	- - -	2230	2230	-	99.5	2.64	2.64
23	I	1.00	18.5	0.226	- - -	2240	2240	-	98.1	2.73	2.73
24	E	1.00	14.8	0.280	- - -	2270	2270	-	95.1	5.56	5.56
25	G	1.00	13.8	0.292	- 100.0 CO_2 -	2200	2200	-	98.0	1.20	1.20
26	E	1.00	14.6	0.266	- 100.0 CO_2 -	2200	2200	-	94.0	1.47	1.47
27	H	1.03	15.4	0.122	varied	-	-	-	90.9	-	-
28	F	1.00	17.5	0.200	varied	2300	2300	-	91.4	-	-
29	I	1.00	17.3	0.197	- 0.14 O_2 0.26 SO_2	-	-	-	4.9	-	-
30	E	1.00	15.0	0.286	1.0 H_2 4 H_2O -	-	2160	0	99.9	-	8.93
31	I	1.00	18.1	0.232	1.7 H_2 4.2 H_2O -	-	2190	0	99.8	-	11.18

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
32	G	1.00	12.8	0.314	1.0 CO	3.4 H_2O	-	-	2200	0	99.9	-	3.85
33	H	1.03	14.6	0.290	1.9 CO	3.5 H_2O	-	-	2200	0	99.9	-	6.45
34	F	1.00	17.2	0.108	3.7 CO	4.0 H_2O	-	2190	2190	2.07	97.8	10.30	10.30
35	E	1.00	15.4	0.253	1.0 CO	-	-	-	2200	0	99.7	-	3.33
36	H	1.03	15.4	0.298	3.9 H_2	3.5 H_2O	-	2180	2180	12.89	88.9	17.24	17.24
37	I	1.00	18.6	0.202	1.1 H_2	-	-	-	2190	4.18	96.1	-	5.72
38	G	1.00	13.3	0.146	2.1 H_2	4 H_2O	0.9 SO_2	-	2170	41.5	59.1	-	5.65
39	G	1.00	14.3	0.152	3.7 CO	7.1 H_2O	-	2190	2190	0.54	99.2	8.51	8.51
40	I	1.00	19.8	0.112[d]	3.5 CO	8.4 H_2O	-	-	2170	6.07	94.1	-	8.78
41	F	1.00	19.7	0.209[d]	3.7 H_2	-	-	2200	2200	38.2	63.0	7.10	7.10
42	H	1.03	16.3	0.324[d]	3.5 H_2	9.9 H_2O	-	2220	2220	14.63	86.3	19.05	19.05
43	E	1.00	15.1	0.308	3.3 H_2	6.0 H_2O	-	-	2160	13.53	87.0	-	20.80
44	G	1.00	13.3	0.198	4.0 CO	3.2 H_2O	-	2190	2190	7.36	92.6	16.68	16.68

[d] -3½+4 mesh.

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
45	I	1.00	18.9	0.102	2.0 CO	3.9 H_2O	-	2230	2230	0.04	99.7	4.59	4.59
46	H	1.03	15.5	0.278	2.2 CO	-	-	-	2270	13.99	87.0	-	5.75
47	F	1.00	18.3	0.099	2.1 CO	-	-	2250	2250	6.44	93.3	3.75	3.75
48	G	1.00	13.6	0.200	3.9 CO	-	-	-	2210	27.25	74.0	-	13.70
49	I	1.00	19.5	0.199	2.0 CO	-	-	-	2250	14.66	85.7	-	4.74
50	G	1.00	13.8	0.300	1.0 CO	-	-	2200	2200	0	98.3	1.72	1.72
51	H	1.03	15.6	0.201	1.0 CO	-	-	2250	2250	0.11	99.1	2.28	2.28
52	F	1.00	18.2	0.101	1.0 CO	-	-	2250	2250	0	99.7	2.02	2.02
53	G	1.00	14.0	0.200	2.0 CO	-	-	-	2000	56.25	37.4	-	0.54
54	H	1.03	16.0	0.278	2.1 CO	-	-	2230	2230	12.98	88.4	6.25	6.25
55	F	1.00	17.8	0.101	1.0 CO	-	-	-	2200	5.85	93.8	-	2.16
56	I	1.00	18.3	0.199	1.9 CO	-	-	2230	2230	17.05	83.7	5.78	5.78
57	F	1.00	16.9	0.099	2.0 CO	-	-	-	2220	12.47	88.2	-	3.26
58	I	1.00	19.1	0.200	1.9 CO	5.2 H_2O	-	-	2210	0	99.8	-	4.59
59	G	1.00	15.0	0.224	1.8 CO	9.0 H_2O	-	2220	2220	0	99.9	5.05	5.05
60	H	1.03	15.8	0.199	4.0 CO	-	-	-	2220	20.8	80.4	-	8.20

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
61	F	1.00	17.6	0.200	1.0 CO	5.0 CO_2	-	2210	2210	0	99.2	2.90	2.90
62	I	1.00	17.3	0.200	2.0 CO	5.0 CO_2	-	-	2220	0	99.9	-	4.56
63	G	1.00	12.6	0.200	3.0 CO	5.0 CO_2	-	-	2200	0	100.0	-	6.81
64	H	1.03	15.2	0.198	4.1 CO	5.1 CO_2	-	-	2190	0	99.8	-	10.31
65	I	1.00	21.7[e]	0.200	3.0 CO	-	-	-	2190	18.91	80.7	-	8.55
66	G	1.00	16.0[e]	0.200	4.0 CO	-	-	-	2240	35.6	67.2	-	8.85
67	H	1.03	18.0[e]	0.198	4.1 CO	5.0 CO_2	-	2170	2170	0.92	98.8	11.50	11.50
68	J	1.00	25.4[e]	0.199	2.1 CO	-	-	-	2230	24.4	77.2	-	4.55
69	K	1.00	25.4[e]	0.200	3.1 CO	5.0 CO_2	-	-	2200	0	99.2	-	9.61
70	G	1.00	14.3[e]	0.199	1.0 CO	-	-	-	2220	0	100.0	-	3.36
71	I	1.00	23.3[e]	0.201	1.0 CO	5.0 CO_2	-	-	2190	0	99.7	-	2.72
72	J	1.00	28.8[e]	0.200	2.0 CO	5.0 CO_2	-	-	2210	0	99.9	-	4.00
73	H	1.03	19.2[e]	0.199	2.0 CO	5.0 CO_2	0.6 SO_2	2220	2210	0.04	99.3	0.98	3.47
74	K	1.00	24.0[e]	0.199	2.0 CO	5.0 CO_2	0.3 SO_2	-	2200	0	100.0	-	4.06

[e] -8+9 mesh anhydrite.

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
75	J	1.00	21.3	0.200	2.0 CO	5.0 CO_2	-	2120	2110	0	99.2	1.70	3.67
76	G	1.00	13.2	0.200	4.0 CO	5.0 CO_2	-	-	2100	24.9	75.8	-	8.62
77	I	1.00	19.1	0.200	2.0 CO	5.0 CO_2	-	2310	2310	0	99.0	3.94	3.94
78	H	1.03	14.7	0.201	4.0 CO	5.0 CO_2	-	2250	2270	0	99.9	3.28	5.14
79	K	1.00	20.6	0.199	2.0 CO	5.0 CO_2	0.3 SO_2	2210	2220	0	99.7	2.12	3.45
80	K	1.00	20.4	0.101	2.0 CO	5.9 CO_2	-	2200	2210	0	99.9	2.77	3.44
81	J	1.00	20.0	0.100	3.0 CO	5.0 CO_2	-	-	2180	0	99.9	-	6.14
82	H	1.03	16.0	0.301	2.0 CO	5.0 CO_2	-	-	2230	0	99.7	-	5.59
83	G	1.00	13.4	0.298	3.0 CO	5.0 CO_2	-	2240	2240	0	100.0	6.41	6.41
84	K	1.00	20.7	0.199	2.0 CO	5.0 CO_2	0.5 SO_2	2220	2210	0	99.9	1.97	2.78
85	H	1.03	15.7	0.299	1.0 CO	5.3 CO_2	-	-	2200	0	99.9	-	3.80
86	L	1.00	17.6	0.100	1.0 CO	5.0 CO_2	-	-	2200	0	100.0	-	2.46
87	J	1.00	19.4	0.100	4.0 CO	5.0 CO_2	-	2170	2170	0.41	99.3	8.70	8.70
88	G	1.00	14.7	0.302	3.0 CO	5.3 CO_2	-	-	2220	0	100.0	-	7.43
89	K	1.00	21.1	0.200	2.0 CO	5.2 CO_2	-	-	2150	0	100.0	-	3.59
90	K	1.00	21.6	0.199	2.0 CO	5.2 CO_2	-	2250	2250	0	98.7	4.17	4.17

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %		Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
91	H	1.03	16.6	0.202	4.0 CO	5.1 CO_2 -	2270	2270	0	99.9	5.21	5.21
92	J	1.00	21.3	0.200	2.0 CO	5.2 CO_2 -	2120	2100	0	99.2	1.35	2.84
93	L	1.00	18.6	0.100	2.0 CO	5.0 CO_2 -	2210	2210	0	99.9	2.82	2.82
94	H	1.03	15.7	0.202	4.0 CO	5.1 CO_2 -	2150	2150	1.08	97.4	10.87	10.87
95	J	1.00	22.2	0.199	2.0 CO	10.0 CO_2 -	2200	2200	0	99.7	3.20	3.20
96	K	1.00	22.8	0.201	2.0 CO	14.9 CO_2 -	2190	2190	0	99.7	3.44	3.44
97	M	1.00	15.7	0.199	4.0 CO	10.0 CO_2 -	2190	2190	0	99.9	11.59	11.59
98	H	1.03	15.8	0.199	4.0 CO	15.0 CO_2 -	2170	2170	0	100.0	9.61	9.61
99A	L	1.00	19.7	0.200	2.0 CO	4.9 CO_2 5.0 SO_2	2220	-	-	-	0.22	-
99B	L	1.00	19.7	0.202	3.0 CO	4.9 CO_2 5.0 SO_2	-	2200	4.12	95.1	-	6.41
100	J	1.00	24.3	0.200	3.0 CO	10.1 CO_2 5.0 SO_2	2210	2200	0.42	99.2	1.23	6.10
101	M	1.00	17.5	0.200	4.0 CO	9.9 CO_2 5.0 SO_2	-	2180	7.11	92.0	-	12.20
102	J	1.00	22.9	0.200	3.0 CO	10.1 CO_2 3.0 SO_2	2210	2190	1.33	98.2	1.17	7.88
103	K	1.00	22.9	0.201	3.0 CO	10.1 CO_2 4.1 SO_2	2220	2180	2.19	98.8	0.98	7.28
104	L	1.00	17.8	0.200	varied		-	-	0	69.6	-	-
105	H	1.03	16.4	0.200	4.0 CO	10.0 CO_2 3.0 SO_2	-	2180	8.55	90.3	-	12.35

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
106	M	1.00	14.9	0.200	4.0 CO	10.0 CO_2	4.0 SO_2	2210	2200	10.42	88.9	2.05	12.35
107	L	1.00	17.2	0.200	3.0 CO	5.0 CO_2	-	-	2200	8.91	91.3	-	8.77
108	J	1.00	21.7	0.201	3.0 CO	10.1 CO_2	2.0 SO_2	2220	2220	0	99.3	1.30	6.85
109	K	1.00	20.5	0.200	3.0 CO	10.1 CO_2	-	-	2190	0	100.0	-	5.75
110	M	1.00	13.4	0.200	3.0 CO	10.0 CO_2	6.0 SO_2	2200	2210	1.35	98.0	0.81	5.56
111	L	1.00	20.5	0.200	3.0 CO	15.0 CO_2	5.0 SO_2	2200	2200	0	99.2	0.77	5.47
112	J	1.00	21.9	0.200	3.0 CO	-	5.0 SO_2	2200	2200	24.8	75.6	0.29	6.10
113	K	1.00	21.2	0.200	3.0 CO	5.1 CO_2	5.0 SO_2	2200	-	1.62	97.8	0.57	5.53
114	N	1.00	9.6	0.200	5.0 CO	5.0 CO_2	-	2190	2190	23.3	78.2	9.93	9.93
115	K	1.00	22.7	0.200	2.0 CO	10.0 CO_2	2.0 SO_2	2200	2200	0.74	98.8	0.24	1.69
116	M	1.00	16.6	0.200	4.0 CO	10.0 CO_2	6.1 SO_2	2210	2190	15.68	84.9	1.62	8.40
117	H	1.03	15.7	0.200	3.0 CO	19.9 CO_2	5.0 SO_2	2200	2200	0	99.7	1.14	5.35
118	J	1.00	24.9	0.200	2.0 CO	10.1 CO_2	3.0 SO_2	2200	2210	0	95.1	0.21	3.00
119	J	1.00	22.1	0.200	2.0 CO	10.0 CO_2	3.0 SO_2	2190	-	0	16.2	0.20	-
120	K	1.00	21.9	0.198	2.0 H_2	8.9 H_2O	2.0 SO_2	2140	2140	22.0	77.0	7.55	7.55
121	H	1.03	16.5	0.200	4.0 H_2	10.1 H_2O	2.0 SO_2	2220	2220	53.8	47.7	9.46	9.46

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
122	L	1.00	20.5	0.200	varied	-	-	77.2	20.1	-	-
123	M	1.00	15.4[f]	0.103	- 1.0 O_2 4.3 SO_2	-	-	0	1.5	-	-
124	M	1.00	16.2[f]	0.100	- 1.0 O_2 2.0 SO_2	-	-	0	2.7	-	-
125	H	1.03	15.1	0.200	3.0 CO 10.0 CO_2 7.0 SO_2	2210	2200	3.78	94.0	0.41	3.30
126	N	1.00	9.0	0.202	5.0 CO 9.7 CO_2 4.9 SO_2	-	2190	40.1	59.6	-	9.44
127	J	1.00	20.9	0.194	2.0 H_2 7.8 H_2O 5.2 SO_2	2130	2130	10.33	90.5	9.92	9.92
128	K	1.00	21.5	0.197	4.1 H_2 8.5 H_2O 5.1 SO_2	2080	2080	36.6	64.9	21.3	21.3
129	M	1.00	16.3	0.196	4.0 H_2 12.9 H_2O 5.1 SO_2	2100	2100	32.9	69.2	25.6	25.6
130	M	1.00	15.9	0.196	2.0 H_2 8.3 H_2O 6.0 SO_2	2140	2140	9.11	91.3	12.20	12.20
131	H	1.03	16.6	0.202	2.0 H_2 7.7 H_2O 6.9 SO_2	2200	2200	12.10	88.8	14.70	14.70
132	K	1.00	20.5	0.194	2.0 H_2 7.6 H_2O 3.1 SO_2	2140	2140	23.3	78.5	11.20	11.20
133	J	1.00	21.9	0.196	2.0 H_2 7.9 H_2O 4.2 SO_2	2120	2120	18.72	82.6	10.97	10.97
134	N	1.00	9.9	0.197	10.0 H_2 9.3 H_2O 10.1 SO_2	-	-	74.8	22.8	-	-

[f] 8 mesh Drierite.

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
135	H	1.03	16.0	0.193	10.2 H_2 6.8 H_2O 5.2 SO_2	-	-	71.1	26.0	-	-
136	M	1.00	16.5	0.20	10 H_2 7-10 H_2O 5 SO_2	-	-	52.4	47.7	-	-
137	M	1.00	14.8	0.200	4.0 CO 9.8 CO_2 2.0 SO_2	2190	2160	21.3	78.9	1.90	12.40
138	N	1.00	9.4	0.200	5.0 CO 19.8 CO_2 5.0 SO_2	-	2190	0	98.6	-	14.10
139	H	1.03	17.0	0.200	4.0 CO 10.0 CO_2 7.0 SO_2	2220	2140	12.15	87.9	2.32	14.70
140	J	1.00	22.0	0.200	varied	-	-	0	22.2	-	-
141	K	1.00	21.0	0.200	3.0 CO 10.1 CO_2 5.0 SO_2	-	-	0	44.9	-	-
142	J	1.00	22.3	0.200	3.0 CO 10.0 CO_2 5.0 SO_2	2200	2140	2.59	97.0	0.99	8.62
143	M	1.00	16.9	0.200	4.0 CO 9.9 CO_2 5.0 SO_2	-	2210	2.27	97.6	-	14.75
144	K	1.00	24.2	0.200	3.0 CO 10.1 CO_2 3.0 SO_2	2210	2160	0.86	98.8	0.91	7.12
145	H	1.03	14.7	0.200	4.0 CO 9.9 CO_2 5.0 SO_2	2170	2130	12.93	85.8	1.37	10.41
146	N	1.00	9.8	0.198	5.1 CO 30.8 CO_2 5.0 SO_2	-	2170	0	99.5	-	12.66
147	M	1.00	17.5	0.199	4.0 CO 19.8 CO_2 5.0 SO_2	2200	2140	0	99.7	2.34	10.90
148	J	1.00	23.3	0.200	3.0 CO - 5.0 SO_2	2210	2150	17.98	83.2	1.26	9.72
149	H	1.03	15.3	0.200	4.0 CO 5.0 CO_2 5.0 SO_2	-	2140	23.20	78.0	-	11.97
150	M	1.00	17.4	0.200	4.0 CO 15.0 CO_2 5.0 SO_2	2210	2160	6.84	93.3	2.44	10.60

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %			Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
151	O	1.00	9.5	0.199	5.0 CO	14.8 CO_2	5.0 SO_2	-	2150	21.0	79.3	-	15.88
152	N	1.00	9.2	0.200	6.0 CO	19.8 CO_2	5.0 SO_2	2170	2170	22.5	87.1	17.9	17.90
153	P	1.00	14.0	0.200	4.0 CO	9.9 CO_2	2.0 SO_2	2210	2200	12.82	83.9	1.43	10.63
154	O	1.00	9.6	0.200	7.0 CO	19.8 CO_2	5.0 SO_2	2160	2160	28.6	71.7	18.92	18.92
155	H	1.03	15.3	0.200	4.0 CO	9.9 CO_2	5.0 SO_2	2120	2100	31.0	68.6	0.54	8.06
156	J	1.00	21.1	0.200	3.0 CO	10.0 CO_2	4.0 SO_2	2210	2180	0	99.5	1.05	7.30
157	P	1.00	15.2	0.200	3.0 CO	9.9 CO_2	6.0 SO_2	2200	2220	0.48	98.1	0.88	4.72
158	M	1.00	16.3	0.200	4.0 CO	9.9 CO_2	5.0 SO_2	2200	2180	9.11	90.9	1.65	13.16
159	O	1.00	9.2	0.200	5.0 CO	10.0 CO_2	5.0 SO_2	-	2170	23.2	75.3	-	24.4
160	P	1.00	15.0	0.200	4.0 CO	9.9 CO_2	6.0 SO_2	2200	-	1.49	97.7	1.49	13.20
161	L	0.50	11.1	0.200	4.0 CO	9.9 CO_2	5.0 SO_2	2100	2120	40.8	59.3	0.40	6.34
162	Q	0.50	12.7	0.200	4.0 CO	10.0 CO_2	5.0 SO_2	2310	-	0.28	98.7	3.24	4.31
163	N	1.00	9.0	0.198	2.1 CO	19.7 CO_2	5.0 SO_2	2200	2200	1.10	97.9	0.30	1.38
164	M	0.50	8.6	0.200	3.0 CO	9.9 CO_2	5.0 SO_2	2210	2210	12.18	87.6	0.78	3.60
165	P	0.50	8.5	0.200	3.0 CO	9.9 CO_2	5.0 SO_2	2210	2210	5.00	93.8	0.84	6.29
166	L	0.50	11.1	0.200	4.0 CO	10.0 CO_2	5.0 SO_2	2200	2160	6.48	93.0	1.92	13.30

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %		Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
167	J	0.50	12.0	0.200	5.0 CO	5.0 CO_2 -	2190	2190	20.9	80.1	15.70	15.70
168	P	1.00	15.3	0.200	2.0 CO	19.8 CO_2 5.0 SO_2	2200	2200	1.79	97.8	0.13	1.18
169	J	1.00	20.1	0.200	2.0 CO	10.0 CO_2 1.0 SO_2	2210	2200	0.59	99.2	0.62	1.43
170	Q	1.00	19.6	0.200	1.0 CO	5.0 CO_2 -	2200	2220	1.16	97.8	1.40	2.42
171	J	1.00	22.8	0.200	2.0 CO	10.0 CO_2 0.5 SO_2	2210	2210	0.71	98.1	0.79	1.73
172	P	1.00	15.6	0.200	2.0 CO	9.9 CO_2 0.5 SO_2	2210	2200	0.03	98.3	1.03	1.53
173	L	1.00	18.7	0.200	2.0 CO	10.0 CO_2 -	2200	2220	0	99.5	2.90	3.76
174	J	0.50	11.9	0.200	5.0 CO	5.0 CO_2 -	2190	2190	23.6	77.2	16.95	16.95
175	Q	0.50	13.1	0.200	4.0 CO	10.0 CO_2 5.0 SO_2	2280	-	1.10	99.5	1.92	-
176	J	1.00	21.6	0.200	3.0 CO	10.0 CO_2 1.0 SO_2	2210	2210	4.54	95.3	2.02	7.94
177	Q	1.00	19.9	0.200	3.0 CO	10.0 CO_2 1.0 SO_2	2210	2210	0	99.4	1.12	7.87
178	L	1.00	18.2	0.200	3.0 CO	10.0 CO_2 2.0 SO_2	2200	-	0.94	98.7	0.60	8.00
179	M	1.00	15.3	0.200	3.0 CO	10.0 CO_2 -	2200	2210	0	99.7	1.45	5.27
180	P	0.50	9.5	0.200	5.0 CO	19.6 CO_2 5.0 SO_2	2200	2170	18.30	82.9	1.98	13.50
181	J	0.50	11.5	0.200	4.0 CO	15.0 CO_2 5.0 SO_2	2210	2190	5.06	94.9	1.84	14.92
182	Q	0.50	11.2	0.200	4.0 CO	5.0 CO_2 5.0 SO_2	2210	-	32.2	68.5	1.47	12.66

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
183	L	0.50	12.2	0.200	5.0 CO 14.9 CO_2 5.0 SO_2	-	2190	27.6	73.6	-	16.58
184	P	0.50	9.8	0.200	4.0 CO 19.7 CO_2 5.0 SO_2	2220	2200	0.71	98.7	1.56	12.86
185	P	0.50	7.2	0.200	3.0 CO 4.9 CO_2 -	2210	2210	5.09	94.0	11.08	11.08
186	N	1.00	9.4	0.200	2.0 CO 9.8 CO_2 2.0 SO_2	2210	2200	0.33	99.1	0.32	1.87
187	O	1.00	9.6	0.200	2.0 CO 9.9 CO_2 1.0 SO_2	2210	2200	0.66	98.7	0.83	1.93
188	N	1.00	9.7	0.200	4.0 CO 9.8 CO_2 5.0 SO_2	2320	2310	5.51	93.1	2.62	3.47
189	Q	1.00	21.2	0.202	2.0 H_2 10.7 H_2O 2.0 SO_2	2100	2100	7.87	92.5	12.0	12.0
190	Q	1.00	23.1	0.199	2.0 H_2 9.3 H_2O 2.0 SO_2	2120	2120	6.68	91.8	11.22	11.22
191	L	1.00	17.9	0.191	2.0 H_2 5.5 H_2O 2.1 SO_2	2140	2140	17.98	81.9	11.90	11.90
192	J	1.00	19.9	0.200	3.0 CO 5.0 CO_2 5.0 SO_2	2210	2190	10.83	88.6	0.51	7.35
193	M	1.00	18.7	0.200	3.0 CO 19.8 CO_2 5.0 SO_2	2220	2190	0	99.0	0.88	5.99
194	Q	1.00	20.7	0.100	2.9 CO 4.9 CO_2 -	-	2170	4.88	95.6	-	6.41
195	J	1.00	18.4	0.099	3.0 CO 19.5 CO_2 5.0 SO_2	2200	2200	0.25	99.4	2.42	5.10
196	N	1.00	10.2	0.300	3.0 CO 20.6 CO_2 5.2 SO_2	2210	2210	0	85.2	0.45	6.50
197	P	1.00	15.9	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	-	2110	11.24	86.5	-	5.89
198	M	1.00	16.5	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	2310	2310	0	44.7	1.32	1.32

Table 18. (Continued)

Run no.	Reactor	Bed depth in.	Charge grams	Mass vel. lb./sec. x ft.^{2}	Gas composition[b] mole %	Temp., °F[a] Initial rate	Temp., °F[a] Max. rate	CaS %	Desulfurization Total %	Desulfurization Rate, %/min. Initial	Desulfurization Rate, %/min. Max.
199	J	1.00	22.9	0.099	3.0 CO 19.5 CO_2 4.9 SO_2	2210	2200	0	99.7	1.93	4.61
200	L	1.00	17.8	0.200	3.0 CO 15.0 CO_2 5.0 SO_2	2220	2210	0	99.2	0.87	5.42
201	P	1.00	15.2[d]	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	2200	-	0	48.7	0.73	-
202	P	1.00	15.5	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	-	2100	11.24	87.3	-	5.75
203	M	1.00	13.4[g]	0.200	3.0 CO 20.0 CO_2 5.0 SO_2	2220	2190	0	99.6	1.03	9.25
204	N	1.00	9.7	0.300	3.0 CO 20.4 CO_2 5.1 SO_2	2210	2200	0	99.4	0.79	6.90
205	P	1.00	14.1[d]	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	2210	2210	0	98.3	1.36	3.74
206	M	1.00	17.3[g]	0.201	3.0 CO 20.2 CO_2 5.1 SO_2	2210	2160	0	99.8	0.88	9.62
207	H	1.03	16.2	0.200	3.0 CO 19.9 CO_2 5.0 SO_2	2300	2300	0	32.5	2.71	2.71
208	Q	1.00	19.4	0.204	3.9 CO 12.2 H_2O 4.9 SO_2	2220	2180	2.24	97.6	4.51	15.93
209	L	1.00	19.3	0.203	3.9 CO 11.6 H_2O 4.9 SO_2	2190	2190	.47	94.7	4.42	12.16

[g] -12+14 mesh